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**PREPARATION AND INVESTIGATION OF  
PHOSPHORS FOR EMISSIVE DISPLAYS**

**FINAL TECHNICAL REPORT**

by

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## **Abstract**

By the use of careful phosphor engineering, new synthetic processes and optimised coating techniques, a range of improved and novel phosphor systems have been developed. These phosphors were designed for cathode ray application, more particularly for low voltage FED use. Improvements include the reduction in particle size to an average of 3 to 1  $\mu\text{m}$  for higher resolution, a new saturated blue low voltage system based on bismuth activated yttrium niobate, and a bright saturated red phosphor barium zinc sulphide manganese. These phosphors were supplied to many US national laboratories and industrial enterprises.

## **Introduction**

The work presented here covers the period from September 1994 to August 1996.

Broadly speaking, the objectives were the preparation of fine particle phosphors, principally for low voltage application and the synthesis of powder and thin films by novel techniques. We emphasised the need for better (greater saturation, higher luminance) blue phosphors. Another aspect of the proposed programme was the investigation of thin film phosphors as little detailed quantitative information was available.

Apart from better colour saturation, the emphasis was on phosphors that would remain stable under high loading conditions. Furthermore, the ever increasing demand for higher resolution dictated the need for finer particles.

It was hoped that the phosphors prepared under this programme would be assessed both by US government establishments and US industrial organisations. Collaboration with laboratories such as Fort Monmouth US Electronics Command, Sandia National Labs., Naval Research Labs and, more especially, the Phosphor Technology Centre of Excellence at Atlanta, Georgia, would be strengthened. Samples of optimised phosphors would be made available to these establishments for assessment, as well as to US industry.

We believe that in nearly all the above objectives, the research programme proved successful, as can be seen from the data provided below.

The report is divided into two principal sections; Section A, the detailed technical report, in which we will present the salient results achieved in this programme; and Section B, which includes a summary of the results and achievements, our conclusions and suggestions for further work. An outline of the report is given on the next page.

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## 1) Literature Survey

It may well be that the years 1994-1995 will be considered a turning point in the resurgence of phosphor research. There can be no doubt that the encouragement received from ARPA in pursuing the development of the better phosphor systems has contributed in a large part to this turn-around. This renewed interest has been marked by a steady increase in publications on phosphor research and also by very large attendances at phosphor sessions and seminars at SID. The team at Greenwich continued its efforts in publicising the importance of phosphors for display technology by presenting a further short course at SID on the fundamentals of emissive displays in June 1994 (1). This was a follow-on from a Workshop presented previously on display phosphors (2). The seminar notes are available on request from the University.

Since the literature on phosphors is so vast, in our literature survey we will confine our attention to cathode ray phosphors and related systems.

It is interesting to note that two books have been published of late which deal in a large part with recent phosphor developments. The first, edited by A H Kitai (3), contains a mixed set of reviews and would provide good background reading in certain areas to newcomers in the field. Although it contains some reviews on electroluminescence, notably DCEL is reviewed by S S Chadha, late of our University, strangely it has very little to say on cathode ray and even less on low voltage phosphors. By contrast, a book by L Ozawa, on the application of cathodoluminescence to display devices (4), deals with many aspects of phosphors for CRT and VF application. It appears to be the first text book that gives details on screening methods and compares in detail the merits of various phosphors under a range of conditions. Unfortunately, it does not deal with low voltage microtip devices, but only with vacuum fluorescent systems. We will only highlight the few aspects pertinent to our investigation. These are:

- 1) The authors affirm that many FED designers state good low voltage CL phosphors have to show good electrical conductance. They maintain that this is not true. The authors then state that the phosphor screen which emits brilliant cathodoluminescence is an insulator and the conductive phosphor screen usually has no cathodoluminescence. Most phosphors are measured in the form of pressed pellets which they suggest show electrical conductivity totally different to that measured on particles in a screen.
- 2) The addition of indium oxide powder, about 20% by weight, to insulating phosphors which render them good, low voltage emitters, does not make the screen conductive. They can put forward no evidence regarding the role of the indium oxide microclusters and suggest that the oxygen vacancies in the indium oxide might act as electron-hole pairs recombination centres.
- 3) They indicate that the type of screen deposited dominates the cathodoluminescent properties. It is suggested that:
  - a) the distribution of the electron shower on the anode is uniform if no phosphor particles are present, but,

- b) the generation of cathodoluminescence is seriously influenced by the condition of the phosphor screen, and,
- c) the aggregated particles do not emit low voltage cathodoluminescence and a thick screen is 'unstable' for generating good emission. They insist that to obtain a brilliant screen, the removal of aggregated particles from the phosphor powder is absolutely necessary,
- d) further, a certain number of holes in the packed screen is necessary. If too many holes are present there will be adhesion problems. It is thus quite clear that the screen has to be prepared with utmost control and a very specific particle size range is needed for best results,
- e) and finally, contamination of phosphor particles with traces of  $\text{In}_2\text{O}_3$  and  $\text{MgO}$  damages the cathodoluminescence under low voltage in the VF displays.

A good review was given by Ronda of the Philips Research Laboratory at the 1994 Electrochemical Society meeting (5). A table of the cathode ray efficiency under low and high energy density excitation was presented, see Table 1.

**Table 1**

White D capability (cathode ray efficiency divided by the y-value of the colour point) of  $\text{ZnS:Ag}$  and  $(\text{La,Gd})\text{O:Br,Ce,Tb}$ , optimised for PTV applications, at low and high excitation density (5).

Phosphor	linear ( $\eta_L/y$ ) (Lm/W)	( $\eta_L/y$ ) at 40 $\text{mJ/cm}^2$ (Lm/W)
$\text{ZnS:Ag}$	230	80
$(\text{La,Gd})\text{O:Br,Ce,Tb}$	135	130

Another interesting aspect of phosphor research summarised by the author is the luminescent characteristics of a number of phosphors under vacuum ultra violet excitation. These are presented in Table 2 overleaf.

**Table 2**

Luminescence characteristics of a number of phosphors under vacuum ultraviolet excitation. For the oxysulphides no quantum efficiency data below about 20eV is available. (E<sub>g</sub>: band gap energy, Min: excitation energy for which quantum efficiency has not been observed has its minimum, P.E: number of photons generated per electron volt excitation energy (5).

Phosphor	E <sub>g</sub> (eV)	Min (eV)	Min/E <sub>g</sub>	P.E. (1/eV)
YVO <sub>4</sub> :Eu	3.7	9.0	2.4	0.075
Zn <sub>2</sub> SiO <sub>4</sub> :Mn	5.5	14.0	2.5	0.07
ZnO:Zn	3.4	9.0	2.6	0.063
Y <sub>2</sub> O <sub>3</sub> :Eu	5.6	14.0	2.5	0.067
ZnS:Ag	3.8	9.0	2.4	0.10
Gd <sub>2</sub> O <sub>2</sub> S:Tb				0.099
Y <sub>2</sub> O <sub>2</sub> S:Eu				0.15
La <sub>5</sub> O <sub>2</sub> S:Eu				0.063

The concept of 'quantum cutters' is brought forward. This idea that under high energy excitation two or more photons can be generated from one excited photon is not new, but the development of phosphors particularly tuned to optimising these processes, may well be one of the salient directions for future phosphor research. Efficient 'quantum cutters' would have many applications. Two immediately spring to mind - they would increase the efficiency of fluorescent lamp phosphors and therefore would prove very attractive for plasma gas devices; furthermore, 'quantum cutters' will be the materials used in non-moving 3D displays. A similar approach is seen in the work of the team at Southampton University, which is developing this type of material in transparent glass form for low-loss fibre communication. The authors here (6) have used ZBLANP glasses for their studies. These are the glasses being investigated by the team in the Naval Laboratories at San Diego for 3D application.

Another interesting application receiving more attention is the development of UV emitting phosphors. Although these are being studied for lamp applications, clearly, they might prove very useful in liquid crystal back lighting systems. The work of the team at Rhone-Poulenc led by Huguenin, on yttrium phosphates, showed promising results (7).

Most phosphor developments, more especially in the lamp industry, are the results of painstaking, very gradual improvements, in the techniques of phosphor synthesis. It has been demonstrated, again by Huguenin et al, that they show far better luminance and efficiency if prepared from mixed oxides (8). Similar systems were developed under the ARPA contract (9) at the University of Greenwich.



The systematic analysis of the phases possible in rare earth silicates, although not specifically devoted to the preparation of phosphors, is also being undertaken (10). The data on  $\text{Ln}_2\text{SiO}_5$  and  $\text{Ln}_2\text{Si}_2\text{O}_7$  could be invaluable in the preparation of more stable, rare earth silicate systems.

Very few papers on luminescent mechanisms pertinent to actual displays or phosphor synthesis, are found in the literature. An exception to this was the study on the mechanism of the luminescence efficiency of  $(\text{LaGd})\text{OBr}:\text{Ce}$  phosphors under CRT excitation (11). This important study points out that powder incorporation of various rare earth substitutes in the host lattice can cause distortion and lead in certain cases to reduction in efficiency due to the increased concentration of killer centres. How the concentrations of certain activators affect the energy charge of electron hole pairs is also discussed. These effects show that, for example, gadolinium to cerium energy transfer cannot be used to increase the efficiency of such systems.

Some specific results pertaining to low voltage CRT zinc oxide are reported by Russian teams (12-16) and also Jacobsen et al at the PTCOE. Although it is very difficult to get precise details, we may summarise the results reported in these publications as indicating that considerable improvements both in efficiency and stability are possible with low voltage zinc oxide phosphors. Thus, efficiencies of up to 8 lumens per watt have been reported which are compared to 3-4 lumens per watt for unmodified material. Various treatments reported are all applied to phosphors already prepared with very controlled stoichiometry. These are described as:

- 1) Modifying zinc oxide with silicone oil followed by surface annealing treatment, with or without gallium salts,
- 2) Modification of the surface of the phosphor with treatments of tungstic oxide ( $\text{WO}_3$ ) and vanadium pentoxide ( $\text{V}_2\text{O}_5$ ).
- 3) The addition of bismuth in small quantities, approximately 0.2%.

It is not clear whether such treatments are specific to zinc oxide only or have been applied more generally to sulphides and oxysulphides, as is claimed by the earlier publication (12). Sulphide treatments are not referred to in subsequent papers.

Very few new phosphor lattice systems have been reported. Clearly, far more emphasis must be placed in future on the development of new lattice systems so that the major improvements still so essential to the display development can be realised. Among the new lattices receiving some attention are the oxynitrides (17). Work on these systems are worthy of detailed study. Recently, methods of synthesising gallium oxynitrides have also been reported (18).

It has been known for some time that to improve the contrast of CRT phosphors, increasing use is being made of ultrafine pigment colour filters placed on the surface of powder colour materials. Some results have recently been reported by a team from Sony Corporation of Japan (19,20). They have used iron oxide for red, zinc oxide titanium nickel cobalt oxide for green, and cobalt aluminium for blue. Although the

effect of the green filter material is limited, the use of both red and blue filter materials show significant improvements in contrast. Likewise, a group from Hitachi Ltd also used a green pigment chromaticity correction in a projection CRT for a HDTV display (21). Possibly of more interest here was the use of a densely packed phosphor screen to reduce light scattering. Further developments with pigment colour filters can clearly be expected. Such systems can be extended both to the new low voltage materials being developed, as well as to thin film systems that may be used in the future.

Ways to improve the efficiency of blue zinc sulphide were analysed by Vigonyailo et al (22). The authors claim best results, with respect to both stability and brightness/efficiency, are obtained by the addition of small quantities, 0.002 weight %, of europium to the standard zinc sulphide phosphors. A summary of the results reported is indicated in Table 3.

**Table 3**

**Illumination-engineering characteristics of ZnS:Eu, Hal  
upon cathode excitation ( $U=14\text{kV}$ ,  $j=1\text{mA/cm}^2$ )**

Luminophor	$B$ , $\text{cd/m}^2$	$x$	$y$
ZnS:Cl	589	0.139	0.085
ZnS:Cl, Eu (0.002 wt %)	624	0.138	0.083
ZnS:Cl, Eu (0.06 wt %) (flux NaCl, $\text{MgCl}_2$ )	532	0.141	0.087
ZnS:Cl	722	0.141	0.086
ZnS:Cl, Eu (0.002 wt %)	779	0.138	0.084
ZnS:Cl, Eu (0.06 wt %) (flux $\text{NH}_4\text{Cl}$ )	638	0.149	0.096
ZnS:Br	787	0.142	0.086
ZnS:Br, Eu (0.002 wt %)	646	0.140	0.089
ZnS:Br, Eu (0.06 wt %)	541	0.140	0.093
ZnS:Ag	464	0.136	0.056

Note:  $B$  is brightness;  $x$ ,  $y$  are the chromatic coordinates

Although considerable further work has been done on the orientation and perfection of thin film zinc oxide (23, 24), publications dealing with orientation studies give little information on the cathodoluminescent properties of the films described. It is quite clear that the nature of the substrate will have a very marked effect on the crystallinity and, hence, the properties of the final film produced.

There is a multitude of literature on the subject of thin films so we have confined ourselves to those areas of particular relevance to our own programme, namely;

- a) aerosol spray pyrolysis of thin film phosphors,
- b) thin film cathodoluminescent phosphors,
- c) the stability of transparent conducting films after exposure to high temperatures.

In a) and b) we are concentrating on oxide phosphors. We have paid only limited attention to sulphides as these are not part of our present terms of reference. It should be noted that the vast majority of publications on thin film phosphors refer to spectral results with brightness and efficiency measurements reported in arbitrary units only. We found no references, with one notable exception, to any description of thin films operating under low voltage cathode ray excitation.

One of the first papers demonstrating the need for high temperature annealing was by Feldman (25), who deposited zinc sulphide on quartz substrates. More recently, yttrium oxide:europium has been deposited by Young et al (26) onto sapphire substrates using magnetron sputtering. The films were 2-3 $\mu$ m thick and were annealed at 1000°C. These were high voltage films so any charge was dissipated by using conventional evaporated aluminium over the phosphor. Schmulovich again dealt with high voltage phosphors (P53-YAGAG:Tb) in his paper in 1989 (27). In his view, transparent thin films can offer high resolution and contrast in applications requiring only moderate brightness, but translucent films are much more attractive in high brightness applications. A variety of methods of preparing CL thin films was described by Wagner et al (28). Zinc oxide, yttrium oxide:europium and YAG:Tb were deposited onto magnesium oxide and sapphire substrates while a GaAsSi substrate was used for zinc sulphide. The efficiency of the films described was much less than the corresponding powder phosphors and no mention of charge build-up was made.

The only papers on aerosol spray pyrolysis for CL films found were those by members of our group at the University of Greenwich (UG), although Falcony (29) did produce a photoluminescent film of Al<sub>2</sub>O<sub>3</sub>:Tb.

With low voltage phosphors, any charge build-up in the film cannot be overcome by applying a front aluminium screen because of its blocking effect on low voltage electrons. One way of accomplishing this is by means of a transparent conducting layer over the substrate. References to transparent conducting films are legion but we have found nothing on their stability after exposure to the high temperatures required for annealing the phosphor films. SnO<sub>2</sub> is much more stable than ITO in this respect. If the conductivity of the tin oxide can be considerably enhanced, it may still retain sufficient conductivity after the annealing process. There are numerous papers on such effects using, for example, fluorine doping in tin oxide by Maruyama and Tabata (30) and fluorine and antimony doping in tin oxide and ITO by Manificier, Fillard and Bind (31).

## 2) Powder Phosphor Developments

### Small Particle RGB Materials

Three fine grain standard CRT phosphors were developed without the use of fluxes thus preventing a build up in concentration of foreign ions in the lattice which may have an adverse effect on the phosphor maintenance. Several techniques for the reduction of the particle size of the phosphors were adopted with emphasis on as little post-firing treatments, especially milling, in order to obtain fine particles. The particle size distribution was monitored using a Coulter Counter. The following protocols have facilitated the production of kilogram quantities of phosphor from highly reproducible smaller batches. These materials have been measured under low voltage cathode ray conditions against commercially available materials.

### Particle Size Reduction

Particle size reduction of the phosphors can be achieved by conventional ball milling. This method will produce fine material ( $<3\mu\text{m}$ ) after prolonged milling times and as a consequence there will be some contamination due to the attrition of the milling balls. This results, however, in considerable loss of luminance/efficiency. An alternative method, McCrone milling, can be used where the mean particle size is reduced without a significant increase in the levels of ultra fine particles and only limited loss of light output. A cross section through the mill jar is represented in Fig. 1. The phosphor powder is ground by impact with the cylindrical surfaces of the milling elements and by shearing between the flat ends of the milling elements between layers. The advantages of this approach are :-

- 1) Obtain  $<3\mu\text{m}$  phosphor without elutriation or sedimentation,
- 2) Particle size distribution is decreased without increasing ultra fine levels,
- 3) High yields compared to conventional methods,
- 4) Reduced contamination.

We found no quantitative results on phosphor using this technique reported in the literature.

### Yttrium Oxide:Europium (P56) - Red

Firing a mixture of yttrium and europium oxides at temperatures of up to  $1600^\circ\text{C}$  without the addition of fluxes, showed an increase in the overall particle size due to aggregation. A co-oxalate method of precipitation was developed which after firing required little treatment to obtain a particle size of  $<3\mu\text{m}$ . This synthetic route followed by a moderate amount of McCrone milling gives yields of 90%. This method has lead to the production of phosphor which is superior to commercially available material under low voltage cathode ray conditions (Fig. 2).

### Yttrium Aluminium Gallium Oxide:Terbium (P53) [YAGAG:Tb] - Green

Although YAGAG:Tb can be produced using the co-oxalate precipitation route firing of a mixture of oxides has been demonstrated to produce a better phosphor. The use of fluxes can be avoided at the expense of firing at higher temperatures. The choice of the type of alumina is critical for the production of high quality phosphor; in this preparation batches produced using gamma alumina were significantly brighter under UV than those produced using the alpha and beta forms. Subsequent testing under low voltage cathode ray conditions again showed superior luminescence compared to commercially available material. Particle size reduction was achieved using McCrone milling and a mean particle size of 3.0-3.2 $\mu$ m obtained (Fig. 3).

### Yttrium Silicate:Cerium (P47) - Blue

Several preparative routes were examined for the preparation of this phosphor. Yttrium and cerium oxalates were co-precipitated in a suspension of colloidal silica. Fine particle phosphor was obtained by two techniques, a) McCrone milling and b) elutriation. Again samples were demonstrated to be superior to commercially available samples as shown in the V/L characteristics in Fig. 4.

### Alternative Preparation Methods

Although McCrone milling is a satisfactory method for particle size reduction it would be preferable to obtain finer bright particles without the need for post furnace treatment. Elutriation of phosphors is laborious and the yields are usually low. Two alternative synthetic pathways using microwave or sol-gel methods are described below.

### Microwave Methods

Three phosphor systems (red, green and blue) have been prepared using a microwave method of production of the precursors. For  $Y_2O_3:Eu$ , precipitation of the co-oxalate of yttrium and europium inside a microwave vessel has led to the production of phosphor which required firing at a reduced temperature compared to the conventional method. Thus these phosphors required a minimum amount of milling in order to obtain a mean particle size <2.5 $\mu$ m. A improvement in the voltage vs luminance characteristics was noted for the microwave derived phosphor compared to commercially available material (Fig. 5).

Yttrium silicate:cerium (P47) precursors were formed by the precipitation of rare earth oxalates in a suspension of either ultra-fine silicic acid or colloidal silica thus producing an oxalate/oxide mixture. Fine particle phosphors with a particle size range 2 $\mu$ m-5 $\mu$ m were produced with a reduced need for milling compared to the conventional synthetic route. However, thus far, no gain in luminance has been obtained using this route compared with commercially available samples.

Development of the method for the synthesis of  $ZnGa_2O_3:Mn$  phosphor using microwave precursors again showed an improvement in the particle size distribution

and the reduced requirement of milling. The reproducibility of this approach was considered to be insufficient for the production of significant sized batches of phosphor.

### Sol-gel Methods

A schematic representation of the sol-gel process can be represented in figure 6 . Essentially the controlled hydrolysis/condensation reaction of precursors produces dimers and then higher ordered structures until a colloidal suspension of particles is obtained. These particles coalesce to form a gel consisting of a viscous network of metal oxide bonds containing trapped solvent molecules. Heating of the gel removes the solvent and allows the metal oxides to densify. Two systems ,  $\text{Y}_2\text{O}_3:\text{Eu}$  and  $\text{Y}_2\text{SiO}_5:\text{Ce}$  , were studied with tetraethyl orthosilicate being used as the  $\text{SiO}_2$  source. Yttrium and rare earth compounds were introduced as an ethanol/water mix. All the reactants were refluxed together and the gelation brought about by increasing the pH using hexamethylenetetramine. The best results were obtained by precipitation in water at pH10 when very fine particles were formed. However, these particles agglomerated on drying. Following firing the phosphors produced by this route were only weakly luminescent compared to those derived by conventional techniques. Clearly, this technique requires considerable improvement and further study, and may prove a useful route to the synthesis of ultra fine particles.

### 3) Novel Blue Systems

#### Bismuth Activated Lattices

Considerable attention has been paid to the development of a new blue low voltage phosphor, with emphasis on the yttrium niobate lattice. Self activated yttrium niobate emits weak cathodoluminescence with a peak at 395nm (Fig. 7). A range of activators, predominantly rare earth oxides, were screened for their potential in the development of this phosphor. The PL was used to discriminate samples without the need for testing under cathode ray conditions. Three samples prepared with activators Bi, Gd and Th showed appreciable blue colour with Bi showing the greatest potential for further exploitation, as shown in Fig. 7.

The effect of varying the concentration of activator on the brightness of the phosphor was studied over the range 0.1%-1.0% Bi wt/wt activator. The optimum concentration was found to be 0.36% Bi wt/wt under 254nm and this was later confirmed by testing under cathode ray conditions at low voltages. The relationship between phosphor brightness, spectral characteristics and the Nb:Y ratio was also investigated. The spectral peak position was found to shift with increasing Nb:Y ratio and additionally a small shift was noted for the higher levels of activator. This relationship can be expressed in Table 1. The cathodoluminescence of these phosphors was also measured against commercially available blue phosphor (P47). The optimum ratio of Nb:Y was found to be 2.5:1. This relationship is summarised in Table 4.

**Table 4**

**Peak Wavelengths for Range of Nb/Y**

Nb/Y	Peak $\lambda$ (nm)	
	0.4% Bi	1.0% Bi
1.0	425	430
1.7	415	415
2.0	425	-
2.5	430	440
3.0	445	450

The strongest CL was obtained with a YNb:Y ratio of 2.5:1 when an efficiency of 0.6 lum/w was obtained. A commercial blue phosphor  $\text{Y}_2\text{SiO}_5\text{:Ce}$  (P47) gave 0.4 lum/watt under the same conditions.

### Particle Size Control

Further studies of this phosphor system with the Nb:Y ratio 2.5:1 and Bi activator concentration 0.36% Bi wt/wt were carried out with the emphasis on controlling and reducing the overall particle size and improving the luminance of the phosphor. Both ball milling and McCrone milling of niobium oxide and of the raw phosphor mixtures were used to reduce the mean particle size to  $<5\mu\text{m}$ . Upon firing, poorly luminescent phosphors were obtained. A possible explanation is that the sample becomes contaminated during the milling process. Fine commercial niobium oxide was obtained but again produced poorly luminescent phosphor. This was attributed to the relatively low purity of the niobium oxide (99.9%). Pre-treatment of the niobium oxide by both acid washing and peroxide washing showed no improvement on the luminance of the phosphor. Yttrium oxide was replaced with yttrium oxalate in the preparation and a range of phosphors produced with the activator concentration of 0.36% Bi wt/wt. Figures 8 and 9 show that this route enables production of phosphor with comparable luminance to those obtained from the mixed oxide method. A mean particle size of  $\sim 7\mu\text{m}$  was obtained but is probably unacceptable for commercial purposes.

Replacement of niobium oxide with an alternative starting material has not yet been achieved. The main problem is firstly in obtaining a suitable stable solution of a niobium species and then of precipitating the niobium in a controlled manner in the form, for example, of a finely divided oxysalt. It can be fused with potassium hydroxide but this unpromising route has yet to be examined. Further, niobium cannot be precipitated as the oxalate (a good precursor for many phosphors) as it forms a water soluble complex.

Finer niobium oxide was obtained from commercial 99.99%  $\text{Nb}_2\text{O}_5$  by two methods, a) elutriation and b) sieving. The latter method is favoured in order to obtain sufficient amounts of material for phosphor preparation. Table 5 shows the comparison of CRT spectra and the CIE coordinates of phosphors produced using finer niobium oxide compared to commercially available phosphor P47.



**Table 5****CIE Co-ordinates for Yttrium Niobate:Bi Phosphors**

<b>Preparation Method</b>	<b>X</b>	<b>Y</b>	<b>Dominant Wavelength (nm)</b>	<b>Peak Wavelength (nm)</b>
Large Batch Yttrium Oxalate/ $\text{Nb}_2\text{O}_5$	0.170	0.178	478.8	440
Large Batch Yttrium Oxide/ $\text{Nb}_2\text{O}_5$	0.169	0.168	477.8	430
Yttrium Oxalate/ Fine Sieved $\text{Nb}_2\text{O}_5$	0.171	0.176	478.5	440
Yttrium Oxalate/ Fine Sieved $\text{Nb}_2\text{O}_5$	0.172	0.185	479	440
Small Batch Yttrium Oxide/ $\text{Nb}_2\text{O}_5$	0.172	0.174	478.2	430
No Activator*	0.169	0.089	465.9	395
P47 Yttrium Silicate:Ce	0.171	0.122	471	395

All preparations Nb:Y ratio 2.5:1 with  $\text{Bi}_2\text{O}_3$  activator 0.4% wt/wt total oxide content, except \*.

In a further method, niobium chloride was used as the starting compound. This is readily hydrolysed to give a fine precipitate of hydrated niobium pentoxide. The chloride was added to a mixed aqueous suspension of yttrium oxalate and bismuth oxide to give a homogeneous suspension of all three components. However poorly luminescent samples resulted.

#### Yttrium Tantalate and Yttrium Niobotantalates

Self activated yttrium tantalate samples prepared with Ta:Y ratios of 1:1 and 2.5:1 showed no PL under @254nm or 366nm excitation, unlike the self activated yttrium niobate which emits a weak blue under 254nm. A comparative study of the yttrium oxide/tantalum oxide system was undertaken with phosphor samples produced for Ta:Y ratios between 1:4 and 4:1 using Bi as an activator. Under UV excitation, the 1Y:1Ta ratio gave the brightest phosphor. Investigation into the relationship between luminance and the activator concentration also showed that the optimum level was 0.36% Bi wt/wt. Yttrium tantalate phosphors showed stronger PL under 366nm

excitation than their niobium based counterparts whereas the converse effect was observed @254nm.

A range of phosphors was prepared with tantalum oxide partially replacing niobium oxide in the preparation where M:Y ratio was 2.5:1 (where M=Nb+Ta). Figure 10 shows that the cathodoluminescence of the phosphors decrease with increasing tantalum concentration. Overall, under low voltage cathode ray conditions (up to 1500V), the brightness of these phosphors can be expressed as :-

Niobates > substituted niobates > tantalates

#### Summary of results

A method has been developed for the production of a blue phosphor which shows improved luminance under low voltage cathode ray conditions compared to commercially available yttrium silicate:cerium phosphor (P47). The optimum level of Bi activator appears to have been found and the relationship between luminance and Nb:Y ratio documented. A degree of control of the particle size distribution of the phosphor has been achieved by using yttrium oxalate to replace yttrium oxide in the preparation. Further reduction in particle size is still needed.

#### 4) Low Voltage Materials

Although as we reported previously (32), ZnO gives good broad luminescence at low voltages, the emission spectrum has only limited application in RGB displays. Furthermore, ZnO shows poor maintenance. The programme was directed at changing the emission colour of the system and improving the maintenance. On the zinc gallate system, some fine tuning was carried out on the manganese activated phosphor and other possible activators were examined. Tin oxide europium was briefly reinvestigated.

##### Substituted ZnO:Zn Phosphors

It was previously noted (32) that substitution of up to 10% of the Zn by Mg in ZnO:Zn powder, causes a shift in spectral emission towards the blue and gives rise to efficient CL. The preparation of this phosphor has been refined using Ar and 90% Ar/10% H<sub>2</sub> as the reductant. When the gas mixture, firing time and firing temperature are rigorously controlled, reproducible batches of the phosphor can now be prepared. The effect of substituting a number of other main group and transition metal oxides from groups II, III and IV was investigated. All, except for the alkaline earth metals, proved harmful, killing the luminescence. Neither calcium nor strontium had a significant effect on the peak wavelength, but calcium tended to kill the luminescence.

The most interesting substituent was barium - a shift in the emission from 504nm to 535nm or 550nm was noted (see Table 6 and Fig. 11). Not unexpectedly, the red shift

**Table 6**

##### **Substituted ZnO:Zn Phosphors**

<b>Phosphor</b>	<b>Luminance/ft-L (@ 1500V, 5<math>\mu</math>A, 1.41 mm diameter spot)</b>	<b>CL peak/nm</b>
(ZnMg)O:Zn	136	475
ZnO:Zn	290	504
ZnBa)O:Zn - low Ba	65	535
(ZnBa)O:Zn - high Ba	30	550

was obtained at the expense of brightness, as shown by the V/L characteristics in Fig. 12. Two methods of synthesis were employed. In the first, the precursor was a mixture of barium nitrate and zinc oxalate, whilst in the second, a co-precipitated barium zinc oxalate was used. In both methods, the final stage involved firing in air unlike the reducing atmosphere employed for ZnO:Zn and (ZnMg)O:Zn. The latter

method gave rise to the phosphor with 550 nm emission and this was thought to indicate a greater incorporation of barium into the lattice than that achieved by the first method. A significant increase in brightness would be required before the barium substituted phosphors would be comparable with the unsubstituted ZnO:Zn phosphor.

A comparison of the shapes of the emission peaks (Fig. 11) shows increasing peak width and asymmetry on going from (Zn,Mg)O:Zn to the red, high Ba, substituted phosphor.

Further work includes incorporation of co-activators, for example Li, Na, although these may lead to sintering. The relationship between Ba incorporation and peak wavelength also needs to be quantified by chemical analysis or XRD methods.

#### Surface modifications of ZnO:Zn

The surface properties of low voltage phosphors, such as ZnO:Zn and (ZnMg)O:Zn, are of vital importance in determining luminescence efficiency. Modifications of the surface therefore, can sometimes improve efficiency (13) either by surface etching or the incorporation of other metals in the surface, or by a combination of the two.

For the ZnO:Zn phosphor, a range of heavy metal atoms was incorporated. These are believed to be confined to the surface and the spectral emission remains unchanged. The most significant improvements were achieved using the heavier atoms (W,Ba), particularly when considering the ageing characteristics. Etching with a solution of  $H_2O_2$  also improved the PL and CL of the ZnO:Zn phosphor. Initial concern as to whether etching was simply removing fine particles was allayed by comparison of the SEMs of etched and unetched phosphor (see photographs 1 and 2).

A combination of Ba- modification and  $H_2O_2$  etching was also considered. A systematic study of five samples of the ZnO:Zn and (ZnMg)O:Zn phosphors, which had been treated as follows, was carried out:

- 1)  $H_2O_2$  etched
- 2) Ba- modified
- 3)  $H_2O_2$  etched then Ba- modified
- 4) Ba- modified then  $H_2O_2$  etched
- 5) Untreated control

The CL measurements for the ZnO:Zn samples indicate that while the untreated sample was initially brightest, all the treated samples show much improved stabilities (see Fig. 13). The Ba- modified sample of (ZnMg)O:Zn was brightest initially, but the modified then etched sample was best after ageing (see Fig. 14).

All modifications improve phosphor stability, however, the conditions for maximum improvement vary from phosphor to phosphor. The differences in brightness of the treated samples, after 15 minutes, are small and may be attributable to variations in the quality and weights of coatings on the tested stubs. However, all show improved brightness when compared to the untreated samples.

## Zinc Gallate Systems

ZnGa<sub>2</sub>O<sub>4</sub>:Mn - The method of preparation of this bright green narrow band phosphor has already been established. Work was concentrated on scaling up, consistent with high quality, by a rigid control of the preparative conditions, particularly at the reduction stage, in order to satisfy a limited commercial demand. A method was also devised to reclaim substandard batches. This involved oxidation followed by re-reduction and enabled the yield based on the high cost Ga<sub>2</sub>O<sub>3</sub> to exceed 90%.

ZnGa<sub>2</sub>O<sub>4</sub> - The blue self-activated phosphor has also been prepared, by a similar method. The CL intensity is much lower than for ZnGa<sub>2</sub>O<sub>4</sub>:Mn or the blue (ZnMg)O:Zn. However, with an emission wavelength of 430nm it is bluer than the (ZnMg)O:Zn (see Fig. 15).

Rare-earth activated ZnGa<sub>2</sub>O<sub>4</sub> - A series of rare-earth impurities was introduced to the lattice and phosphors were prepared under both oxidising and reducing conditions. In the oxidised state only the Eu<sup>III</sup> phosphor showed any significant CL emission, but this was of lower intensity than found for other Eu<sup>III</sup> phosphors. Only the Gd activated phosphor showed any noticeable emission in the reduced state, but this was no more intense than the self-activated phosphor.

Transition metal activated ZnGa<sub>2</sub>O<sub>4</sub> - A number of transition metal activators were also tried. These included Bi, Pb, Mo and W. Neither Mo or W activators produced any PL while the Bi activated phosphor showed only a very pale blue luminance. The most interesting addition was Pb which, after reduction, showed a greenish or blue luminescence. A detailed investigation of this phosphor has yet to yield a set of conditions under which one or the other emissions can be consistently obtained. The system appears to be very sensitive to preparation temperature and compositional fluctuations and also to variations in the reducing atmosphere. The blue emission may, in fact, result from the self-activated phosphor suggesting that the volatility of the Pb-salt may be a problem.

## Tin Oxide:Europium

As there was still some interest in this phosphor by industry, it was briefly re-investigated. Preparation was carried out via the fluxed mixed oxide route, in which tin (IV) and europium oxides and alkaline earth chloride fluxes are intimately mixed by milling in 2-propanol. After an initial firing at 1500°C, more flux is added and the mixture is refired at the same temperature. The high firing temperatures are required to obtain significant luminance. The product is acid washed to remove the flux and to provide some comminution.

The particle size of the washed material is around 7-8µm and milling is required to reduce this for many applications. This results in a weakening of the PL, but any loss can be regained by a short high temperature annealing, with little increase in particle size. The final material produced is still inefficient (V/L and I/L characteristics in Figs. 16 and 17) and there is a spectral emission shift compared to the normal Eu<sup>III</sup> emission. Further modifications to the preparation may be required to improve efficiency.

## 5) Sulphide Phosphors

It has not yet been established whether sulphide phosphors are compatible with low voltage electron emitters. Therefore, these systems were initially not investigated. However, upon an industrial request for a bright red phosphor, the  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  system was investigated.

### Barium Zinc Sulphide:Manganese

The potential of the  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  phosphor was recognised at Greenwich in the early 1970s (33, 34). In 1976, Fau et al (35) claimed a relative CRT brightness of the  $\alpha$ -form of the material of 154% of the commercially used rare-earth oxysulphide phosphor,  $\text{Y}_2\text{O}_2\text{S:Eu}$ . Recently, we have re-investigated the  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  system for low voltage application. The phosphor was prepared using a novel method, developed here. This involves co-precipitation of barium, zinc and manganese salts, the sulphur being introduced as a solution in hydrazine hydrate. The mixture is subsequently fired at a temperature around 800°C in an inert atmosphere.

The phosphor shows a bright red photoluminescence under 366nm. The V/L and I/L characteristics from the preliminary low voltage CL measurements are shown in Figs. 18 and 19. Fig. 20 shows the CL emission spectrum with the peak at 630nm.

The red emission peak and the brightness obtained indicates that in systems that are stable in the presence of sulphide,  $\text{Ba}_2\text{ZnS}_3$  is one of the best red emitting phosphor developed so far.

## 6) Phosphor Deposition Methods

The CL characteristics of a phosphor are determined on a thin layer of the powder deposited on an SEM stub. We developed a standard method involving electrophoretic deposition of the phosphor suspended in a very dilute solution of an electrolyte ( $\text{Al}(\text{NO}_3)_3$ ) in 2-propanol. The stub acts as the cathode with a stainless steel anode and a voltage of 150V is applied usually for 1-5 minutes. It has been found that the quality and weight of the coating show unacceptable variation from one phosphor to another and also between different batches of the same phosphor.

In an attempt to elucidate and improve this process, a range of variables has been considered. These are:

- 1) Phosphor type
- 2) Phosphor concentration (wt/vol electrolyte)
- 3) Electrolyte concentration
- 4) Electrolyte type ( $\text{Al}(\text{NO}_3)_3$  and  $\text{Mg}(\text{NO}_3)_2$ )
- 5) Voltage applied
- 6) Deposition time
- 7) Age of suspension
- 8) Effect of gravity (settling)

It has become clear that no one set of conditions is applicable to all phosphors. However, settling by gravity alone can be successfully used to coat a range of phosphors, and this is about as widely applicable as the standard method outlined above.

## 7) Thin Films

### a) Simple Layer Structures

During our two year research, significant progress has been made in producing bright, luminescent thin films using aerosol spray pyrolysis (ASP) techniques. Most of the precursors were of organometallic compounds dissolved in organic solvents. The system, as shown in Fig. 21, was initially used but it proved very difficult to produce even films over an area greater than about 1cm x 1cm. The system was therefore modified. The use of a peristaltic pump ensured better control of the liquid flow to the nebuliser in order to produce a fine mist spray over the substrates. The mist reservoir and reaction chamber were abandoned and, instead, the spray mist was passed directly over the substrates, which are heated to a temperature between 430°C and 470°C. This method provided a much increased film growth rate about 100nm/min. and importantly, gave even films.

The preparation of bright, luminescent thin films not only relies on the precursors and the spraying method used, but relies heavily on the annealing conditions. The annealing procedure determines, to a great extent, the type of substrate employed. For these phosphors whose annealing temperature is around 1000°C, quartz substrates are sufficient, while some films have to be annealed above 1300°C, for which sapphire substrates are needed. In the past two years, thin film phosphors of ZnO:Zn, (Zn,Mg)O:Zn, Y<sub>2</sub>O<sub>3</sub>:Eu, SnO<sub>2</sub>:Eu, YAG:Tb, YAGAG:Tb, YNbO<sub>4</sub>:Bi as well as ZnGa<sub>2</sub>O<sub>4</sub>:Mn, Y<sub>2</sub>SiO<sub>5</sub>:Ce were investigated. The results are discussed as follows.

#### ZnO:Zn films

Zn acetylacetonate (acac)<sub>2</sub> solutions in a mixed organic solvent were sprayed on to quartz substrates. The films were annealed in a reducing atmosphere at 1000°C. The thickness of the films was estimated from the internodal separation of a UV/VIS scan combined with examination of SEM photograph. A range of films was prepared varying in thickness between 150nm and 2µm. Above 1 µm, the opacity of the films increased rapidly and a double layer structure is present. The thicker layers tend to be powdery showing poor adhesion; the top layer can be separated from the layer that adheres to the substrate. This is clearly evident from Photograph 3. It has been established that this remaining layer still shows CL. The V/L plot over the range of thickness is shown in Fig. 22 and this result demonstrates that even the thinnest films exhibit luminescence. For the thickest films (>2µm) at high current densities, luminance values exceeding 1000ft.L have been recorded (Fig. 23).

#### YAG:Tb and YAGAG:Tb thin films

Thin films of both Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Tb (YAG) and Y<sub>3</sub>(Al/Ga)<sub>5</sub>O<sub>12</sub>:Tb (YAGAG) were produced from a precursor solution of the acac's of the major elements (Y, Al and Ga) and Tb acetate in acetone/methoxyethanol. Annealing temperatures around 1500°C under an air ambient were necessary in order to produce any significant luminescence. At this high temperature, sapphire substrates were used.



The colour and intensity of the emission depended both upon the Tb concentration and the Al/Ga ratio, similar to the observations reported for powders by Ohno and Abe (36). For low Tb levels, the emission is distinctly blue (Fig. 24). As the Tb concentration is increased, it can be seen that the colour changes to green/yellow. There is also some rearrangement of the spectral power when Al is partially replaced by Ga, as shown in Fig. 25.

Although the intensity of the CL is stronger at high Tb levels, it is unstable, showing distinct hysteresis during measurement of CL characteristics. After prolonged ageing at 1500V and 5 $\mu$ A, some stability was achieved. The instability in the film is not understood. Charging effects cannot fully account for it, as the degradation is irreversible. It is possibly due to the presence of an impurity, most likely sodium, in the aluminium or gallium acac precursors which would be carried over into the film. YAGAG:Tb films of varying thickness from 0.15 $\mu$ m to 1.2 $\mu$ m were produced. The L/V characteristics of these films are represented in Fig. 26. The efficiency of these films was calculated to be 0.21 L/W for YAGAG:Tb and 0.15L/W for YAG:Tb.

#### Y<sub>2</sub>O<sub>3</sub>:Eu thin films

Good quality films were produced using very dilute solutions of Y(acac)<sub>3</sub> and Eu acetate precursors which resulted in a much finer mist. A programmed annealing procedure was also carried out to ensure good adhesion to the sapphire substrate.

The luminance values of films from 0.15 $\mu$ m up to 2 $\mu$ m are illustrated in Fig. 27. From these results, there was no evidence of a 'dead' layer, even the thinnest layers showing some luminescence at voltages as low as 400V. The efficiency results calculated for these films was 0.27L/W.

#### SnO<sub>2</sub>:Eu thin films

SnO<sub>2</sub>:Eu(III) films were also produced using ASP. The precursors used were di-n-butyltin diacetate (DBTDA) and Eu acetate. Sapphire substrates were used so as to withstand the annealing temperatures of 1500°C. An oxidising atmosphere was employed. Bright orange luminescence was produced and the CL characteristics are shown in Fig.28 .

#### YNbO<sub>4</sub>:Bi thin films

No niobate phosphor thin films have been reported in the literature. In view of our results on the powder, a thin film study was initiated. Simple layer films of YNbO<sub>4</sub>:Bi were prepared using precursors or Y(acac)<sub>3</sub>, Nb(V) ethoxide and Bi nitrate in an acetone/methoxyethanol mixture. The annealing temperatures again were high, so sapphire substrates were employed. Unlike other phosphor films, air annealing did not produce evenly bright films. An embedding technique was introduced instead. This proved very successful as the quality of films was improved dramatically. Evenly opaque films with a dominant peak at 430nm were obtained. YNbO<sub>4</sub>:Bi powder phosphor was used as embedding matrix. Fig. 29 shows the I/L characteristic of the films.

## Other Phosphor Films

Initial investigations were carried out on other possible thin film systems, including  $\text{Y}_2\text{O}_3:\text{Bi}$ ,  $\text{YNbO}_4:\text{Nd}$ ,  $\text{ZnGa}_2\text{O}_4$ ,  $\text{ZnGaO}_4:\text{Mn}$ ,  $\text{CaTiO}_3:\text{Pr}$  and  $\text{Y}_2\text{SiO}_5:\text{Ce}$  (P47). For  $\text{Y}_2\text{O}_3:\text{Bi}$ ,  $\text{YNbO}_4:\text{Nd}$  and  $\text{ZnGa}_2\text{O}_4$ , poor blue luminescence was observed. For  $\text{CaTiO}_3:\text{Pr}$ , no solvent compatible with both the calcium and titanium precursors was found. With  $\text{Y}_2\text{SiO}_5:\text{Ce}$ , both Y (acac) and tetraethyl orthosilicate (TEOS) are readily soluble in an acetone/2-methoxyethanol mixture, but the film produced did not show luminescence; this could be due to the high volatility of the TEOS. We have achieved green luminescence from the  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  thin films, but further research into the annealing conditions needs to be undertaken.

### **b) Multilayer Structures**

It was proposed that for low voltage CL, if a conducting interlayer could be introduced between phosphor layer and substrate, the conducting layer may prevent the build-up of static charge on the phosphor surface and lead to increased CL efficiency.

$\text{SnO}_2$  is a well-known conductor; however, its conductivity is degraded at the high annealing temperatures we use. Experiments indicated that fluoride introduced into  $\text{SnO}_2$  layer, by adding  $\text{NH}_4\text{HF}_2$  to the precursor solution, increases and stabilises the conductivity. The effect of fluoride is demonstrated in Fig. 30 showing that there is a ten fold increase in conductivity compared with the undoped  $\text{SnO}_2$ . After annealing at temperatures greater than  $1000^\circ\text{C}$ , the F doped films are still about four times as conducting as the equivalent undoped films.

For comparing the CL characteristics, both simple layers and multilayers were built up on common substrates as shown in Fig. 31. A mask was used to cover the control section during the initial  $\text{SnO}_2$  deposition. However, investigations both here and at the ARL Fort Monmouth, demonstrated that diffusion of  $\text{SnO}_2$  took place during spraying and/or annealing, and a 'clean' control was not obtained. This is evident in the SIMS analysis in Fig. 32 of a  $\text{ZnO}$  multilayer showing some diffusion between the interlayer and phosphor. Diffusion was easily avoided by using separate substrates, for the simple and multilayer structures. The influence of  $\text{SnO}_2$  and  $\text{SnO}_2(\text{F})$  interlayers on several thin film phosphors was investigated as described below.

### $\text{ZnO}:\text{Zn}/\text{SnO}_2$ and $\text{ZnO}:\text{Zn}/\text{SnO}_2(\text{F})$ Systems

The CL characteristics of a simple layer of  $\text{ZnO}:\text{Zn}$  and multilayers of  $\text{ZnO}:\text{Zn}$  with interlayers of  $\text{SnO}_2$  and  $\text{SnO}_2(\text{F})$  are represented in Fig. 33. For both thickness of phosphor layers ( $0.15\mu\text{m}$  and  $0.45\mu\text{m}$ ), an interlayer of  $\text{SnO}_2$  or  $\text{SnO}_2(\text{F})$  improves the luminance of  $\text{ZnO}:\text{Zn}$ . The optimum thickness for  $\text{SnO}_2$  or  $\text{SnO}_2(\text{F})$  was found to be  $0.5\mu\text{m}$ . At all voltages, the brightness order is:

$\text{SnO}_2(\text{F})$  interlayer >  $\text{SnO}_2$  interlayer > simple layer.

### YAGAG:Tb/ SnO<sub>2</sub> and YAGAG:Tb/ SnO<sub>2</sub>(F) Systems

Interlayers of both SnO<sub>2</sub> and SnO<sub>2</sub>(F) were introduced between YAGAG:Tb and sapphire substrates. The phosphor layers of YAGAG:Tb were 0.3µm and 1.2µm thick. The V/L plots were similar to those found for ZnO:Zn, again the F doped interlayer yielding the most efficient phosphor film.

### Y<sub>2</sub>O<sub>3</sub>:Eu/ SnO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>:Eu/SnO<sub>2</sub>(F) Systems

The multilayer systems were also utilised for Y<sub>2</sub>O<sub>3</sub>:Eu thin film phosphor. As well as SnO<sub>2</sub> and F doped SnO<sub>2</sub>, an insulating interlayer of ZrO<sub>2</sub> was also used. The V/L characteristics for a 0.6mm phosphor film combined with 0.5mm interlayer are shown in Fig. 34. Undoped SnO<sub>2</sub> and ZrO<sub>2</sub> interlayers were also significantly bright than the simple films, this could be due to a volume effect. Again, the SnO<sub>2</sub>(F) interlayer yielded the most efficient film.

In summary, it is evident for all the cases considered that for thin films, the introduction of an interlayer enhances the CL. Further, the greatest increase was found where the interlayer retained significant conductivity after the annealing stage, thus, presumably preventing the build up of static charge on the phosphor surface. But even slightly or non-conducting interlayers gave some increase in CL intensity. This is ascribed to a 'volume' effect.

### **c) Aqueous Aerosol Spray Pyrolysis**

Previously we reported significant progress in the preparation of luminescent ZnO:Zn thin films using ASP. Films were prepared using organometallic zinc compounds dissolved in organic solvents. The films showed the characteristic blue-green luminescence with a dominant peak at 505nm. The methods used were extended to aqueous solutions using either zinc nitrate or zinc acetate precursors. Opaque and even films were produced. Fig. 35 demonstrates that the films prepared using aqueous precursors were as bright or brighter than those produced with organometallic precursors.

Future investigations should be aimed at understanding the electron penetration through the phosphor thin film. This might explain why the interlayer improves the brightness of the phosphor thin film. Further investigations into lattices such as YNbO<sub>4</sub>:Bi and ZnGa<sub>2</sub>O<sub>4</sub>:Mn should be carried out to improve their luminance output. This could be achieved by changing the precursor concentration and the solvents used. Aqueous precursor spraying has produced remarkable results from the ZnO:Zn phosphor thin film. An investigation into other phosphor lattices using aqueous ASP routes should be undertaken.

## 8) Cathodoluminescence Measurements

All cathodoluminescent data reported was carried out on the cathodoluminescent measurement low voltage system with its associated spectral measurement equipment. This will now be described.

### The low voltage, 400-5000V system

All phosphors are assessed using the low voltage demountable system. It is based on a Kimball Physics gun (EFG-7), capable of 400-5000 eV excitation at up to 200  $\mu$ A emission current, with a minimum spot size of 1.41mm dia. This gun is housed in a stainless steel chamber containing five exit ports (70 mm external dia). To reach minimum pressure of  $10^{-8}$  torr, a backing rotary and a turbo pump are used. Two gauges monitor the pressure in the system. The first, a Pirani gauge, monitors down to  $10^{-3}$  torr, and the second, an ionising gauge, displays the pressure down to  $10^{-8}$  torr. It is baked out using an external heating tape in series with a PID controller/indicator.

To assess the phosphor brightness, a manipulator was installed with an aluminium multi sample holder with a Faraday cup attachment. This enabled up to six samples to be accommodated in the vacuum chamber, and has considerably accelerated the throughput of samples for measurement. The manipulator has 360° of rotation and travel of an inch. This allows for the Faraday cup to be interchanged with the phosphor screen. The phosphor screens are at an angle of 45° from the gun to the measurement window. A Gamma Telephotometer is used for luminance measurements over a range of voltage and current conditions. Current is accurately measured by utilising the Faraday cup within the chamber.

In order to standardise measurements phosphor powder samples have been exchanged between the ARL at Fort Monmouth and ourselves for characterisation. Good agreement was reached between the two groups when identical source current and voltage settings were used. However using the Faraday cup, measurements were an order of magnitude lower than the source current. To increase the versatility of the luminance measurements a pulse electron beam system was also installed.

We will shortly be able to measure the rise and decay time of all phosphors. We will also assess the phosphors for the most suitable pulse rate for specific applications.

A high voltage system is also being set up.

### The High Voltage System

The high vacuum system has been installed but the teething troubles with the rotary pumps have yet to be overcome. This is a much larger system than the low voltage one, with access flanges of 200 and 150mm compared with 70mm. It is also more versatile, provided with more manipulative facilities for the samples. Conversely, because of its size and the use of diffusion pumps (not turbo pumps), it takes longer to evacuate, with a higher probability of leaks.

The vacuum system consists of a stainless steel body separated into two independently pumped compartments by a manual gate valve. The smaller compartment serves as an antechamber for loading workpieces into the system. At present it is fitted with a horizontal motorised manipulator arm. Each compartment has its own diffusion/rotary pump provision and the main vacuum chamber has an added titanium sublimation pump. In normal operation, the system is capable of reaching  $10^{-9}$  torr but with the sublimation pump back up, it can reach  $10^{-10}$  torr. There is a gate valve system which allows the main chamber to remain under vacuum during sample changes. There are several view ports on the system, all at strategic locations, to allow full observation and also an additional vertically mounted x-y-z manipulator. An electron gun, with a capability of 20keV and incorporating a raster provision, has been purchased from Kimball Physics and is awaiting installation.

#### The associated spectral and chromaticity systems

A PC controlled spectrometer is used for spectral analysis. This is based around a 0.5m Bentham monochromator with a 1200line/mm grating and photomultiplier detector. The system is IEEE based and driven by dedicated commercial software. The spectrometer is capable of measuring spectra over a range of 350-850nm with a resolution of 1nm. The system is regularly calibrated using the Bentham SRS8 standard source.

The system can also yield chromaticity and film thickness information. For chromaticity and spectral information a flexible light guide is used to collect light from the cathodoluminescent equipment. The film thickness measurement system utilises a self reflecting light guide that is butted to the sample to estimate film thickness from the interference fringes in the spectrum.

#### **Summary**

During this ARPA contract, a variety of bright phosphor thin films have been produced. Table 7 summarises the luminescent properties for a selection of simple films produced using organometallic precursors.

**Table 7**

#### **Summary of thin film phosphors**

Phosphor	Activator content (wt%)	Colour	Main Peak (nm)	Luminance (ft-L) 1500V&320 $\mu$ A/cm <sup>2</sup>
ZnO:Zn	self activated	greenish-blue	504	135
Y <sub>2</sub> O <sub>3</sub> :Eu	5	red	610	86
YAG:Tb	3.25	bluish-green		47
YAGAG:Tb	6.5	Green		65
SnO <sub>2</sub> :Eu	1.25	orange red	588	24
YNbO <sub>4</sub> :Bi	0.4	blue	430	13

## **9) Collaboration**

We have had considerable interchange of data and measurement technologies with US government bodies, more especially the team at Fort Monmouth, Sandia Laboratories, as well as the Naval Research Laboratory in Washington, but we have received very little information from US industry. Although we have supplied substantial quantities of phosphors to a range of companies, with one notable exception, very little data on the materials supplied has been forthcoming. We have also initiated exchange of samples and measurements with the Phosphor Centre of Excellence and hope, in the future, to set up a collaborative programme with the phosphor teams in Atlanta. During the period of this contract 4.1 kg of powder phosphors and 80 phosphor thin films were distributed amongst twelve US organisations.

## Section B - Summary of Results and Future Work

### 10) Conclusions

The programme carried out can be divided roughly into the development of fine powders and thin films.

#### I) Powders

##### a) Improved particle size distribution

As we pointed out in our introduction, one of the principal objectives of the programme was the development of a range of techniques for the preparation of powder phosphors with an ideal particle size of  $1\mu\text{m}$ . Clearly, every phosphor system has its own chemistry and synthetic procedures and therefore, in certain cases, the preparation of fine particle phosphors is relatively easy, while in others, it presents a challenge to the phosphor chemist. For example, the methods developed for the synthesis of the broad emitting  $\text{ZnO}:\text{Zn}$  yields phosphors of the order of  $1\mu\text{m}$ , while standard synthetic processes used for the synthesis of sulphides yield materials between  $7$  and  $10\mu\text{m}$ . A similar particle size is obtained when using standard preparative methods for a range of oxides. By careful control or removal of fluxes, heating techniques, the use of microwave methods and McCrone milling, we have achieved a useful fine particle range for most of the phosphor systems investigated. Broadly speaking, we are confident that we can now produce phosphors in the  $3\mu\text{m}$  particle range and with further modification, the size of these can be reduced. We have achieved these results without the appreciable degradation usually encountered by conventional grinding or milling techniques. A typical result is indicated in Fig. 36 showing the particle distribution of phosphors obtained at the beginning of our programme, and those which can now be achieved.

##### b) New phosphor developments

We decided on three methods of approach:

##### 1) Novel phosphor engineering

In devising a new phosphor system the general criteria are known. These include, stability under high loading, low voltage operation and good colour saturation. The systematic examination of stable oxide phosphor systems led us to Bi doped yttrium niobates. We hoped that transition metal activators would yield efficient systems and we obtained a good saturated blue emitter. Similar phosphors had been tried for lamp phosphor application but were not very efficient, no previous optimisation for low voltage FED applications was found.

## 2) New synthetic methods

Many practical phosphor systems which are used industrially are still synthesised by methods developed over thirty years ago. We used new synthetic routes. This approach has led to a very promising red  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  system.

## 3) Surface etching and coating treatments

For low voltage systems where the electron penetration is very limited, the condition of the surface is critical. Here we improved the stability of  $\text{ZnO:Zn}$  phosphors by surface treatment involving the addition of heavy metals. The effect of similar treatments on refractory oxides still needs considerable study.

The general improvement of powder phosphors can be evaluated by inspection of Table 8. It should be stressed that no suitable saturated blue phosphor operating at low voltage was available at the start of the programme. We have developed yttrium niobate lattices doped with bismuth showing good blue saturation. We have also made considerable strides in the development of powder phosphors showing good saturated red emission.

**Table 8**

### **Fine Powders Status for Low Voltage Application**

		<b>*ft-L Start of Contract</b>	<b>*ft-L Finish of Contract</b>
<u>Blue</u>	$\text{Y}_2\text{SiO}_5\text{:Ce}$	82	116
	Y niobate:bismuth	New - no data	168
<u>Green</u>	YAGAG:Tb	210	325
	$\text{ZnGa}_2\text{O}_4\text{:Mn}$	261	270
<u>Red</u>	$\text{Y}_2\text{O}_3\text{:Eu}$	360	465
	$\text{Ba}_2\text{ZnS}_3\text{:Mn}$	New - no data	310

\*Measured at 1500V 320 $\mu\text{A cm}^{-2}$

\*The start of contract values are the brightest values we obtained from our samples or fine commercial powder.



The results recently obtained on  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  indicate that providing that sulphides do not attack the electron emitting surface, we can now fill a most important need in the development of low voltage phosphors. The brightness and saturation characteristics of this phosphor are adequate for most practical applications.

## II) Thin Films

As we have shown in our literature survey, we have found very few references in the literature which included practical quantitative data on thin film phosphors operating at low voltages. Table 9 indicates the progress we have made in the development of such thin film phosphors. Clearly, further progress must be made in the development of blue thin films, but we have demonstrated the possibility of three colour thin film devices. It should be stressed, however, that although patterning and deposition techniques for making multicoloured phosphor powder screens are readily available from the cathode ray industry, the preparation of RGB thin films still presents considerable practical difficulties. So far, only high temperature treatment of the thin films has yielded promising results. The development of practical three colour high resolution thin film systems therefore, still requires considerable effort. However, the preparation of monochrome or possible two colour thin film high resolution systems for head-up displays or camcorders is now a practical possibility. With the aerosol spray technology that we have developed, it would not be too difficult to mass-produce screens 1 or 2 cm in diameter for this type of application. Such screens would have the brightness and high resolution possibilities that are needed.

**Table 9**

### **Thin Films Status for Low Voltage Application**

		<b>ft-L Start of Contract*</b>	<b>ft-L Finish of Contract</b>
<u>Blue</u>	$\text{YNbO}_4\text{:Bi}$	New - no data	13
<u>Green</u>	$\text{YAGAG:Tb}$	5.5 (YAG)	65
	$\text{ZnGa}_2\text{O}_4\text{:Mn}$	2	12.5
	$\text{ZnO}$	66	135
<u>Red</u>	$\text{Y}_2\text{O}_3\text{:Eu}$	31	86
	$\text{SnO}_2\text{:Eu}$	3.4	24

\*Measured at 1500V 320 $\mu\text{A cm}^{-2}$

### III) Measurements

Although our measurement techniques for the ranges 400V-3000V are adequate, it should be emphasised that during this programme very little work was done in the ranges 0-300V and 3000V and above. Equipment to determine the property of phosphors under these conditions are being set up.

It should be emphasised that under practical conditions it is most probably that displays will be operated under a pulsed mode. It is well known that low voltage systems can be operated at a very undemanding refresh rate. Thus, phosphors with suitable rise and decay characteristics can be used at low voltages. Unfortunately, we have only just begun our measurements of the new phosphor systems under pulsed conditions.

### **Future Work**

#### a) Phosphor synthesis

We believe that the hydrazine hydrate-sulphur method we have developed for the synthesis of systems such as barium zinc sulphide can be extended to a whole group of sulphides such as the thiogallates and other binary and ternary sulphides. We hope to explore this method and investigate its possibilities for phosphor synthesis. Clearly, we have been very encouraged with our results so far on barium zinc sulphide.

We believe from other work we have carried out at the University of Greenwich on the preparation of phosphors by sol-gel techniques, that this method must be explored further, more especially when fine particle phosphors are required.

The surface treatment, more especially of highly refractive phosphors, as well as the alteration of the surface by the inclusion of heavy metals which has proved so successful with the zinc oxide, must be extended to more refractory phosphor systems. Clearly, etching techniques must also be developed for the more refractory materials and novel etching systems will have to be considered.

We will also extend some of our techniques, which were developed for the preparation of thin films by aerosol pyrolysis, for the preparation of nanoparticles. We have just started a programme with the University of Colorado under ARPA support, to study these systems further.

#### b) Measurements

We hope to extend our measurement techniques to the whole voltage range from 0-20,000V and apparatus is now being set up at Greenwich to carry out such measurements. Clearly, all future measurements will have to be carried out under both direct and pulsed conditions.

#### c) Collaborations

Although we have progressed in our collaboration with both American government and academic establishments in the measurement assessment and interchange of results

on phosphors, we are most disappointed in the lack of interchange we have had with US industry. Although our contacts with Fort Monmouth and Sandia have resulted in joint publications (37, 38) and fruitful discussions with the Naval Research Laboratory has led to the exchange of ideas on nanoparticles and fundamental studies, our interaction with US industry has been disappointing. Although industry is ready to receive samples from us, very little information has been forthcoming. It is hoped, in the not-too-distant future, to rectify this situation. Little progress will be made in the development of phosphors if phosphors are not assessed in practical devices, and a reiterative programme between the research on the materials and its use in devices is not forthcoming.

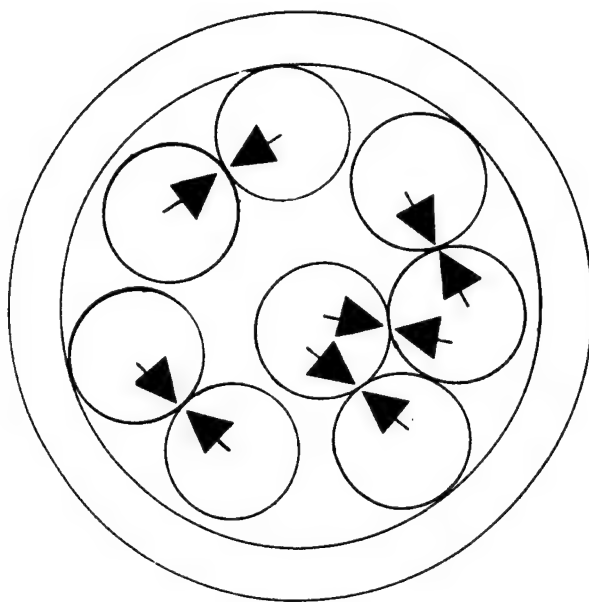
We believe that our work on both powders and thin films has demonstrated the real possibility of multicoloured, low voltage display devices. Powder devices are now possible showing good emission in all three colours. Thin film devices are now practical for monochrome application and further work is required to yield RGB systems.

## 11) References

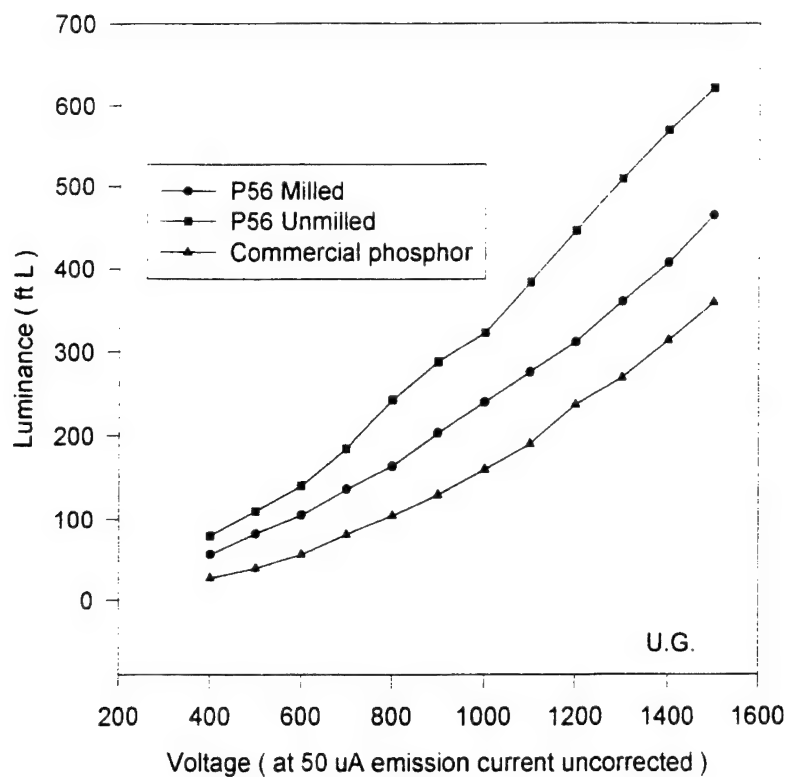
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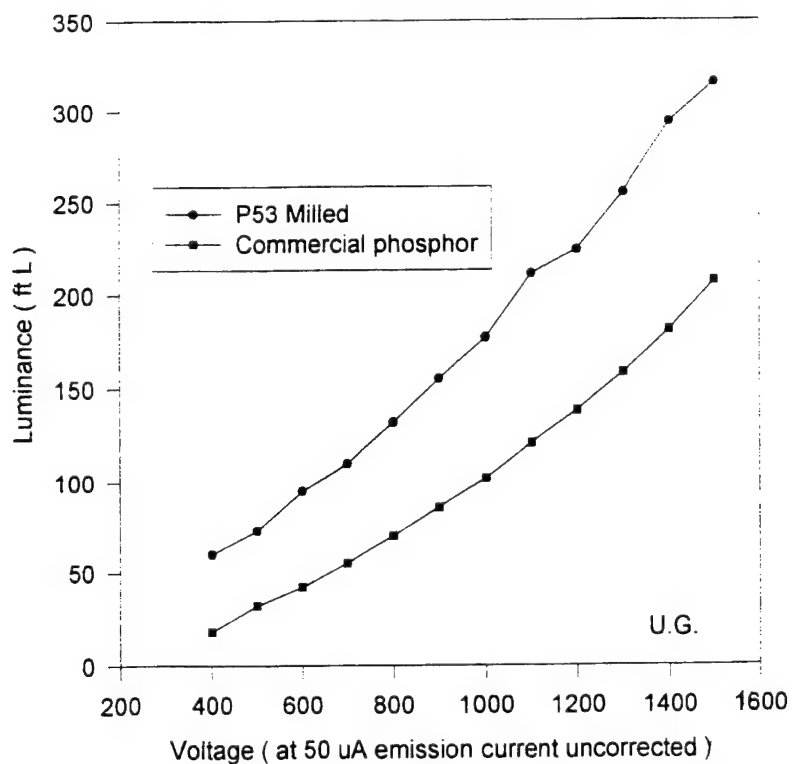
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**Fig. 1 Cross section of a McCrone grinding jar**

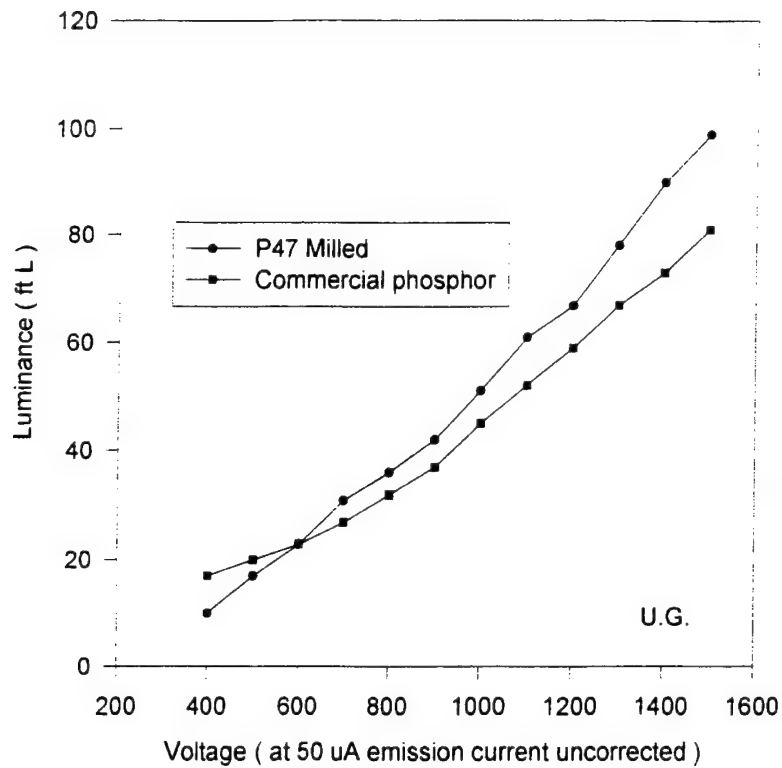


**Fig. 2** V/L characteristics for  $\text{Y}_2\text{O}_3:\text{Eu}$  (P56)

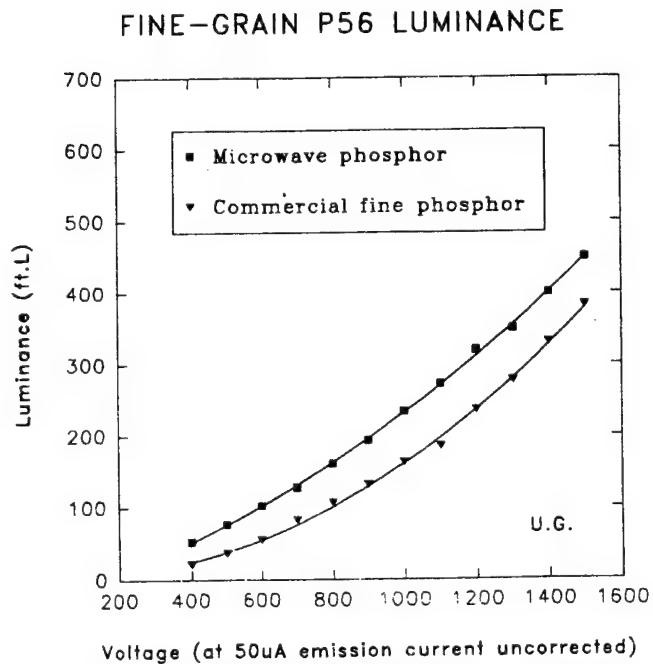


**Fig. 3** V/L characteristics for  $\text{Y}_3(\text{Al/Ga})_5\text{O}_{12}:\text{Tb}$  (P53)





**Fig. 4 V/L Characteristics for  $\text{Y}_2\text{SiO}_5:\text{Ce}$  (P47)**



**Fig. 5 V/L Characteristics for  $\text{Y}_2\text{O}_3:\text{Eu}$  (P56)**

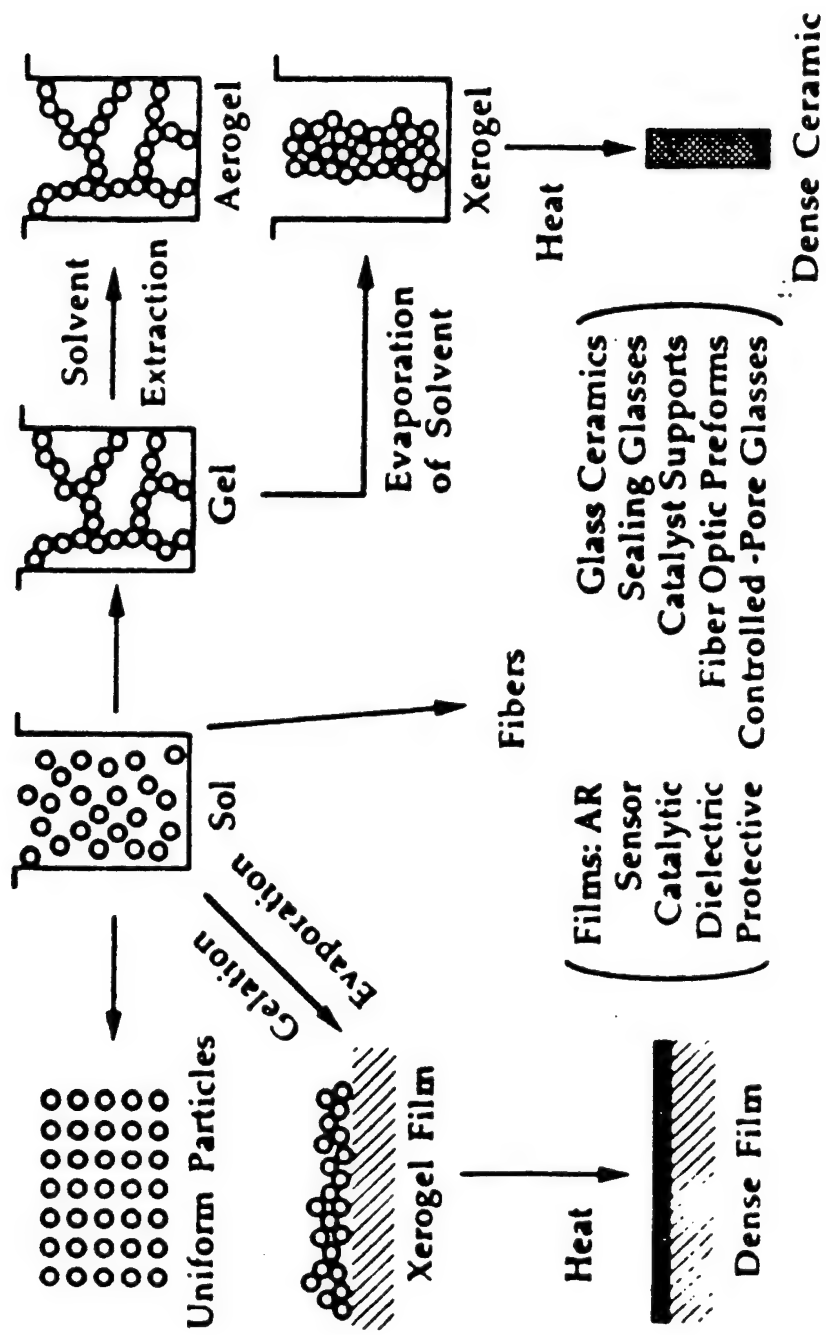
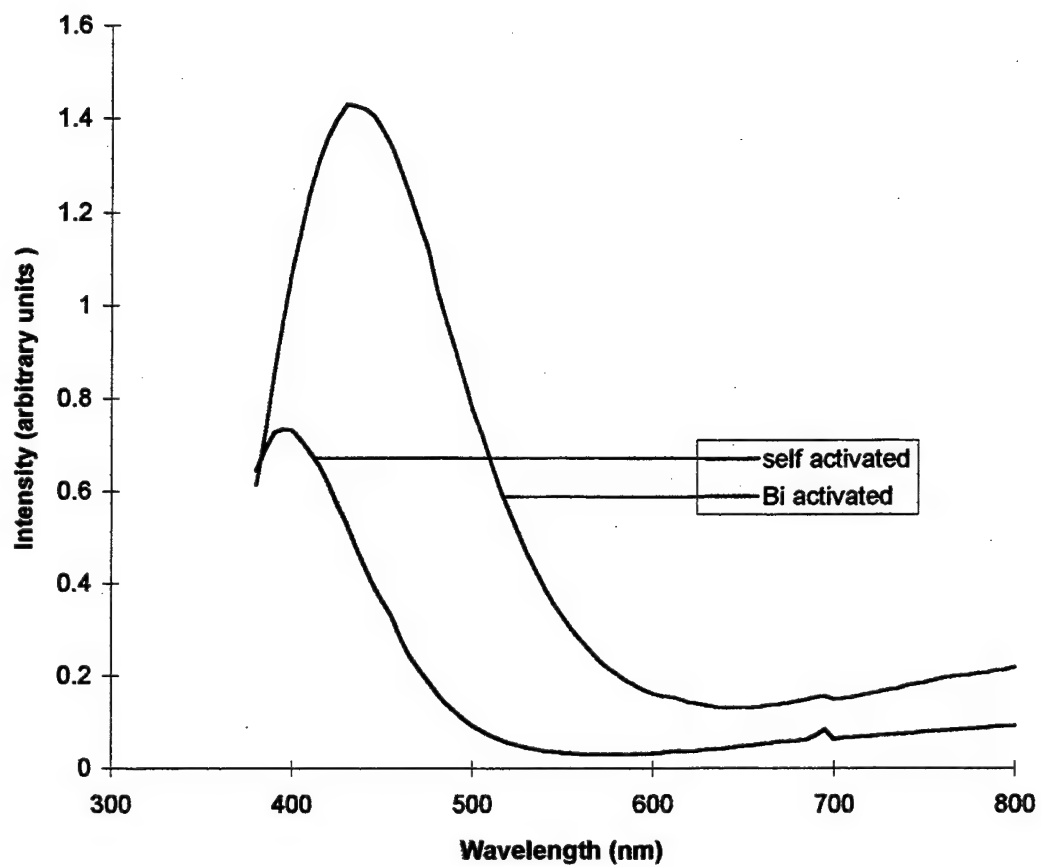
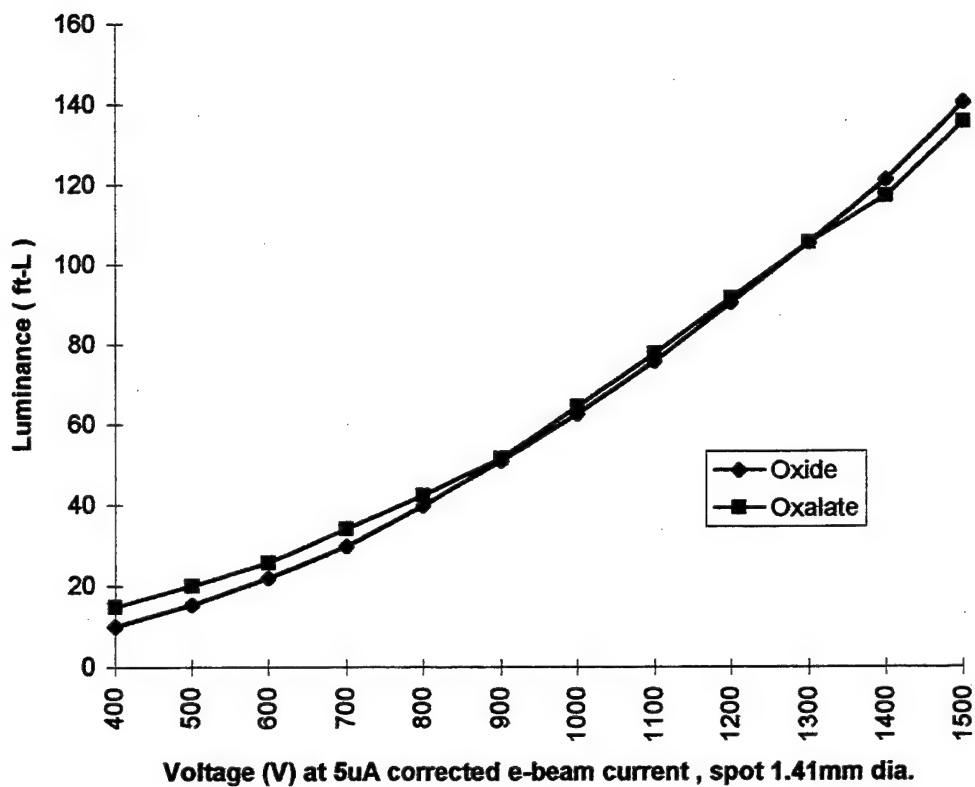


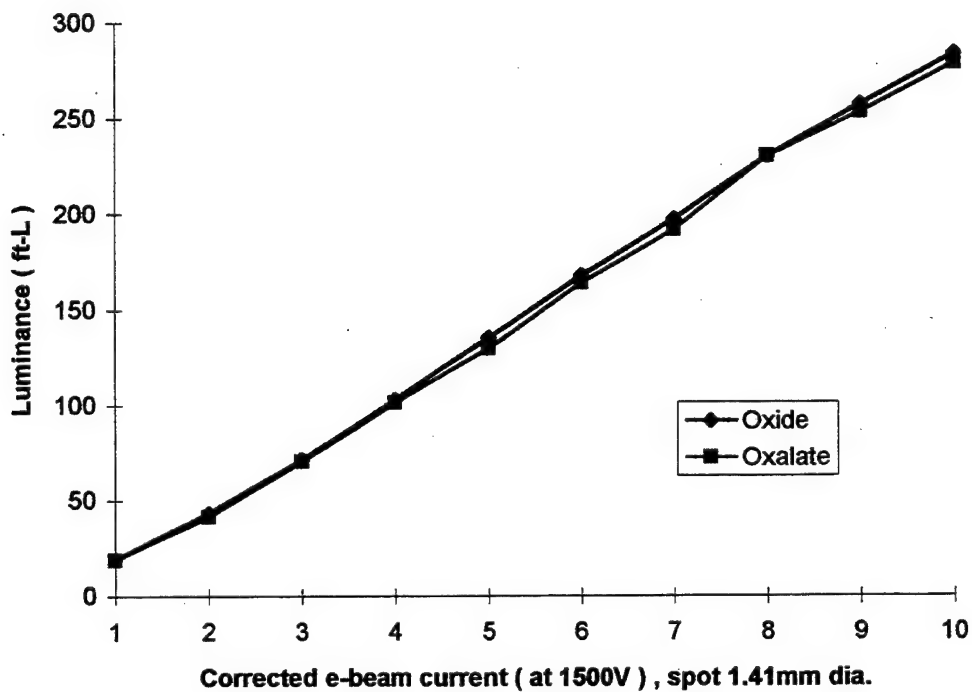
Figure 6 : Overview of the sol-gel process



**Fig. 7 C/L Spectra for yttrium niobate phosphors**



**Fig 8:V/L Characteristics for Yttrium Niobate : Bismuth**



**Fig 9 :I/L Characteristics for Yttrium Niobate : Bismuth**

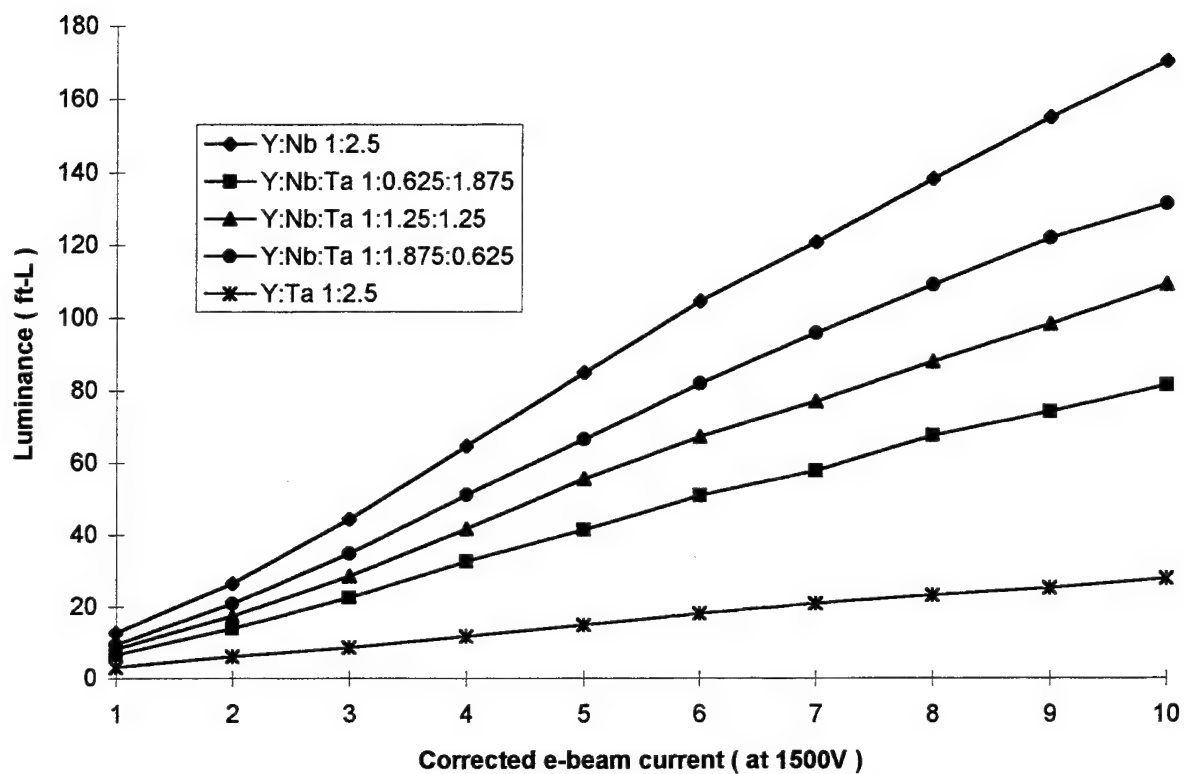
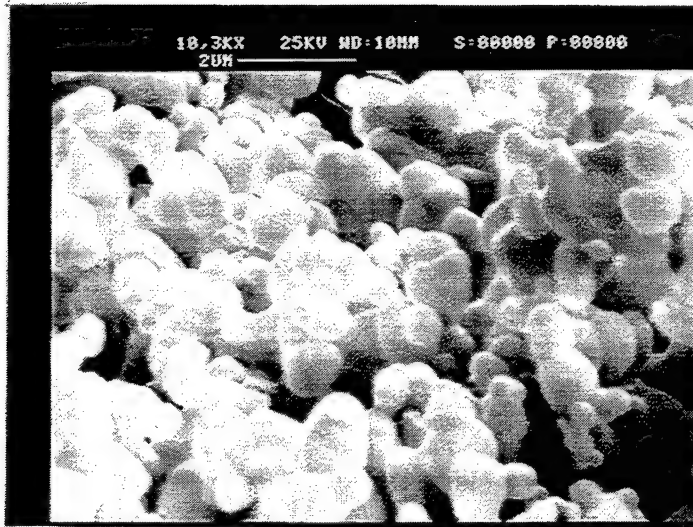


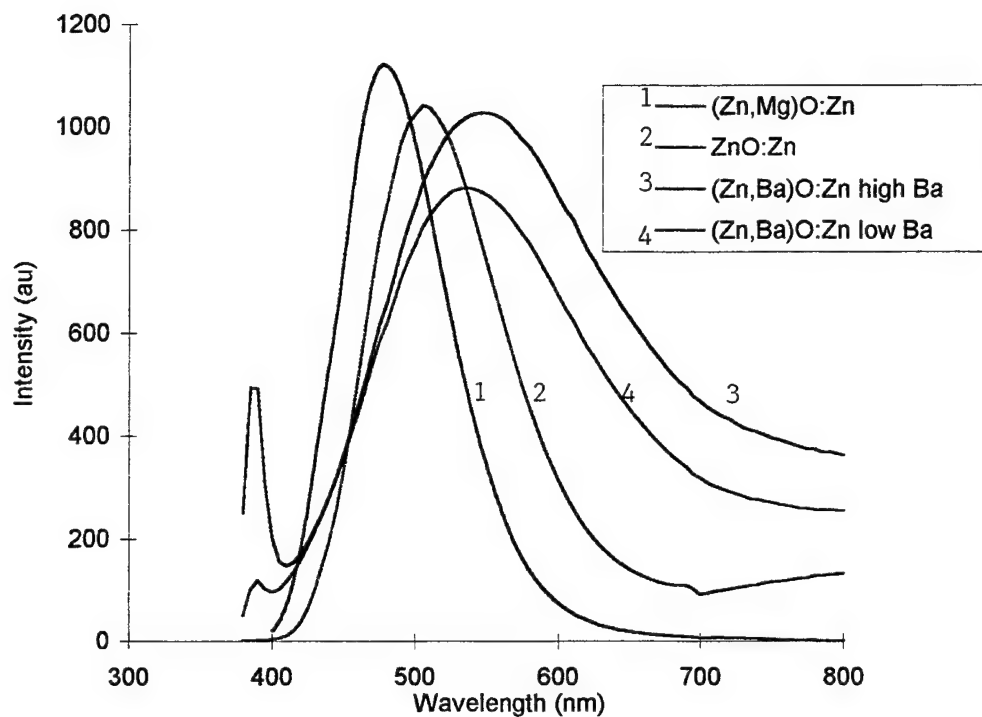
Fig 10 :Niobium oxide substitution of yttrium tantalate phosphors.



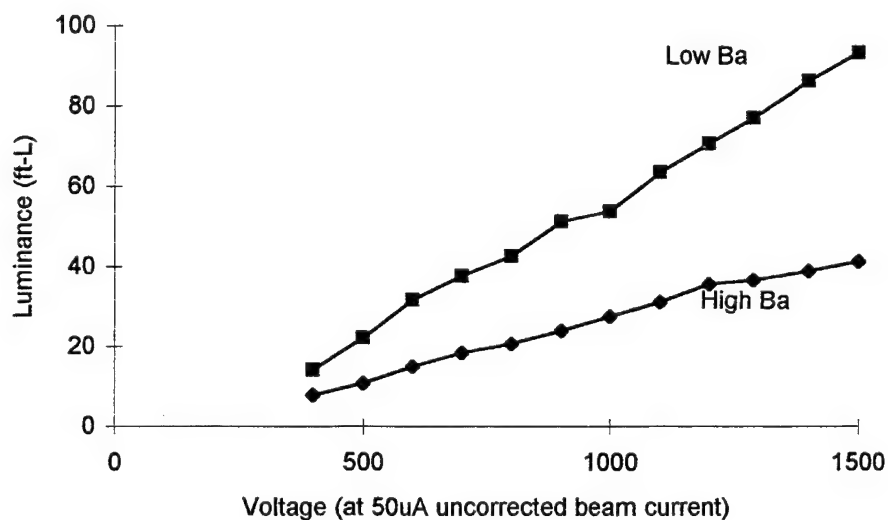
Photograph 1 Standard ZnO:Zn phosphor



Photograph 2 H<sub>2</sub>O<sub>2</sub> etched ZnO:Zn phosphor



**Fig. 11** Spectral emission of substituted ZnO:Zn phosphors



**Fig. 12** V/L characteristics of (Zn,Ba)O:Zn

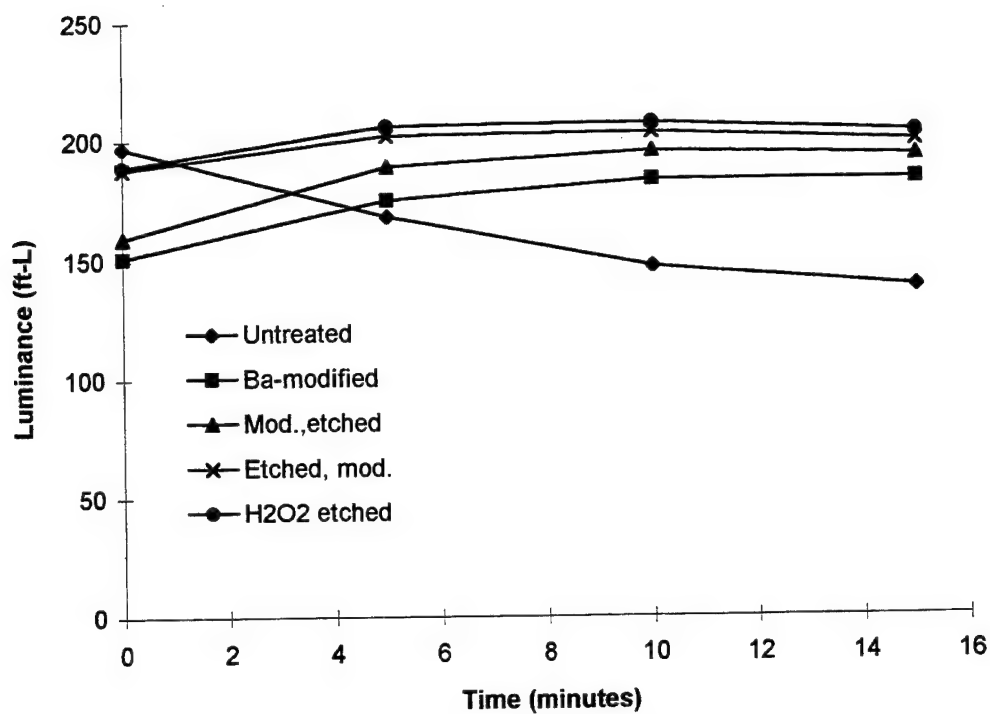


Fig. 13. Life Test for ZnO:Zn Phosphors at 1500V, 5μA.

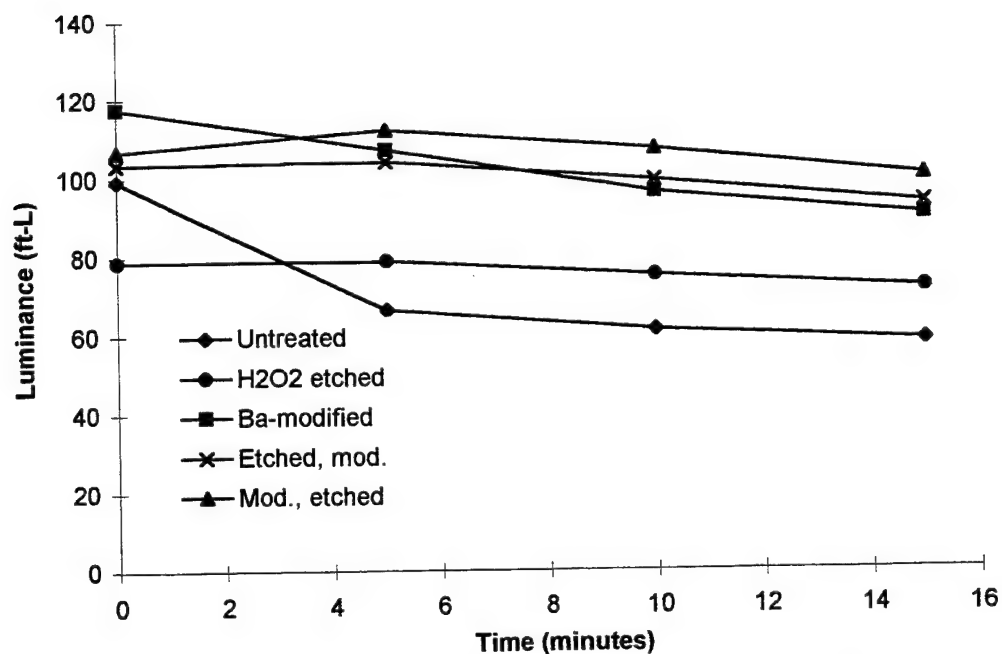


Fig.14. Life Test for (Zn,Mg)O:Zn Phosphors, at 1500V, 5μA.



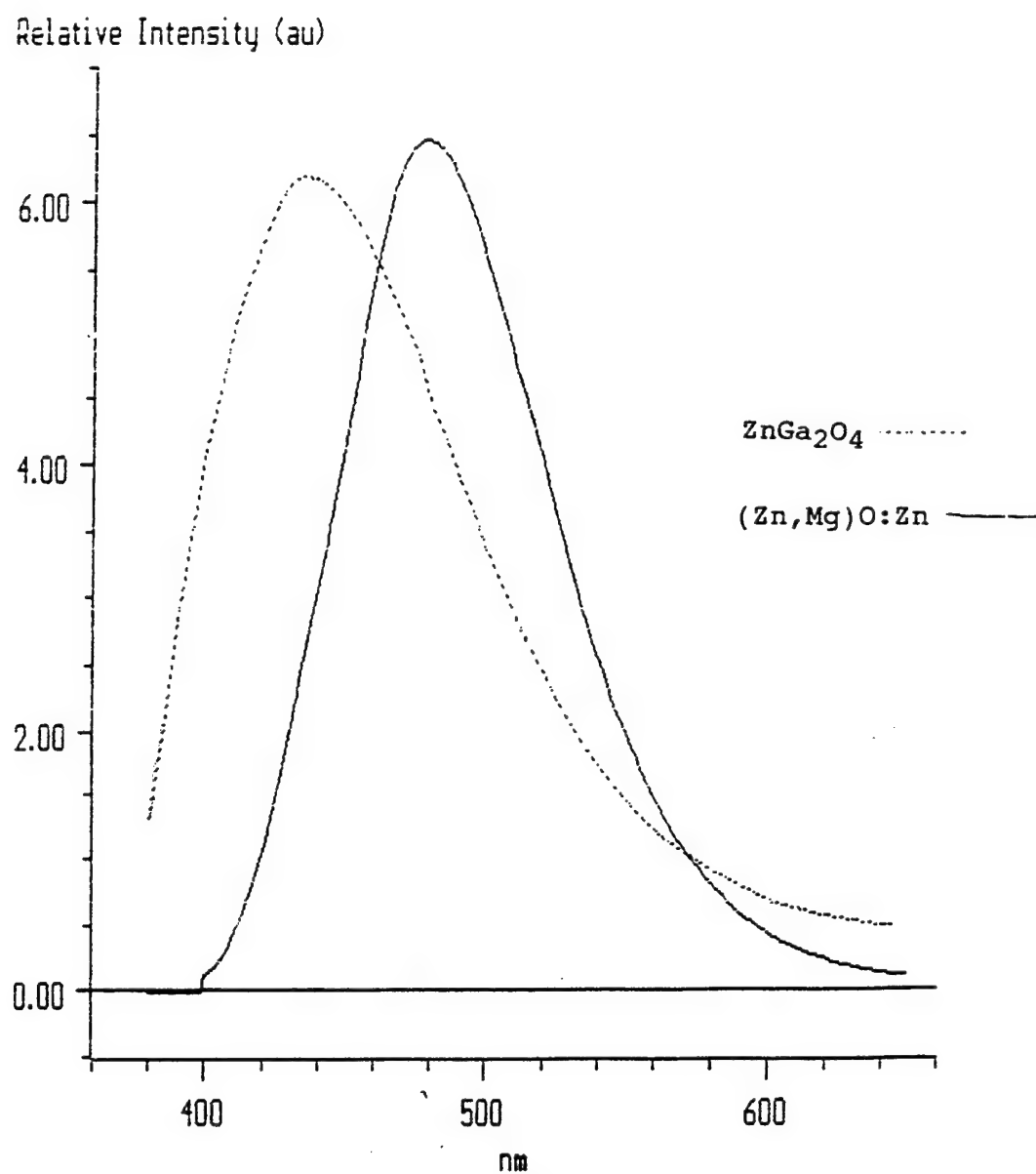


Fig. 15 CL spectral emission of  $\text{ZnGa}_2\text{O}_4$  and  $(\text{Zn,Mg})\text{O}:\text{Zn}$

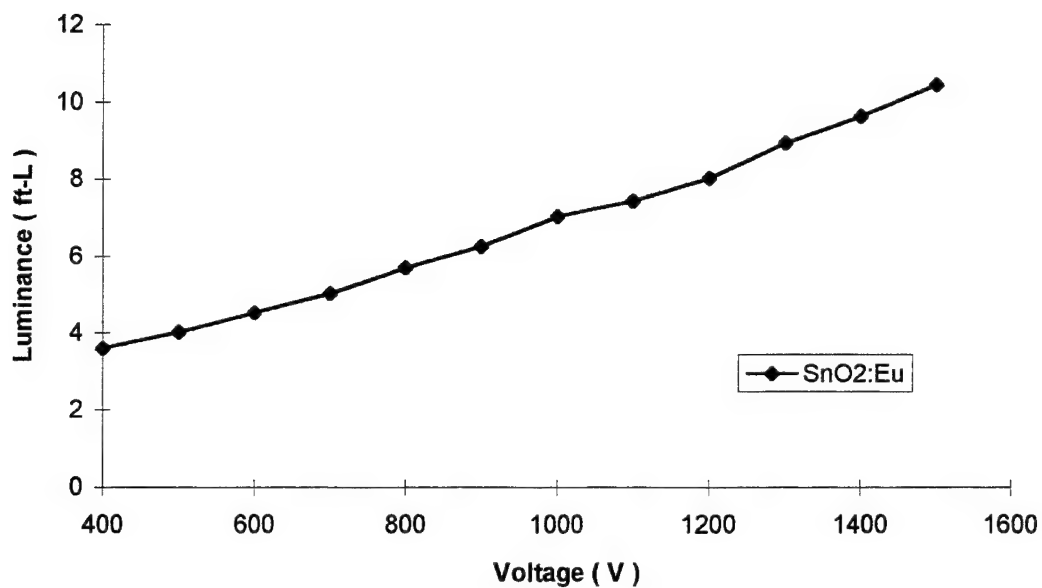


Fig. 16 V/L of SnO<sub>2</sub>:Eu, beam current 5 $\mu$ A, e-beam 1.41mm dia.

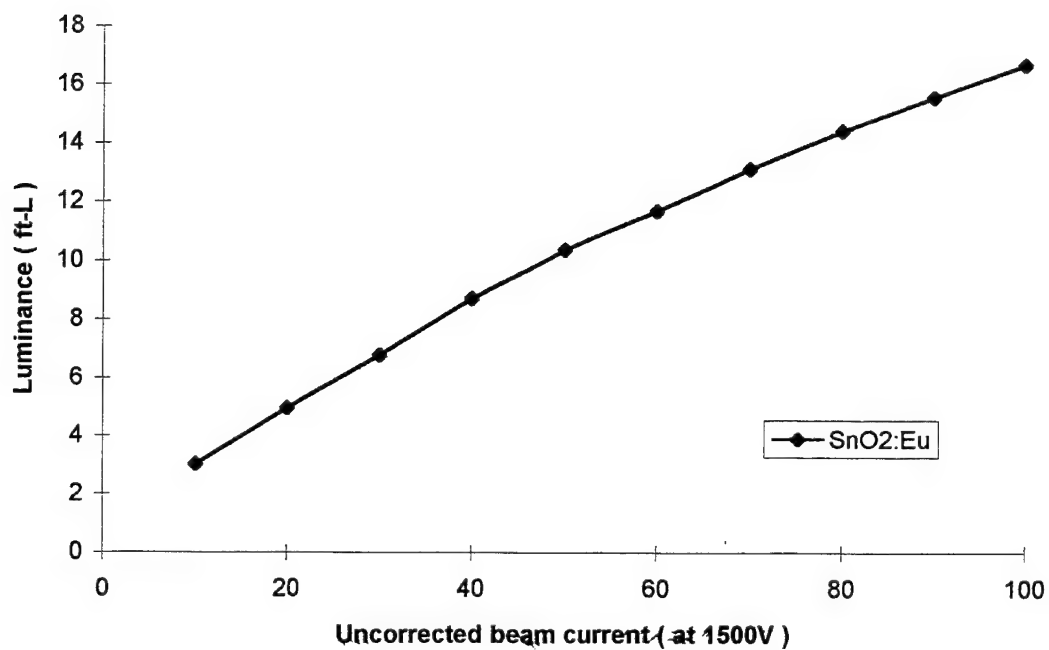
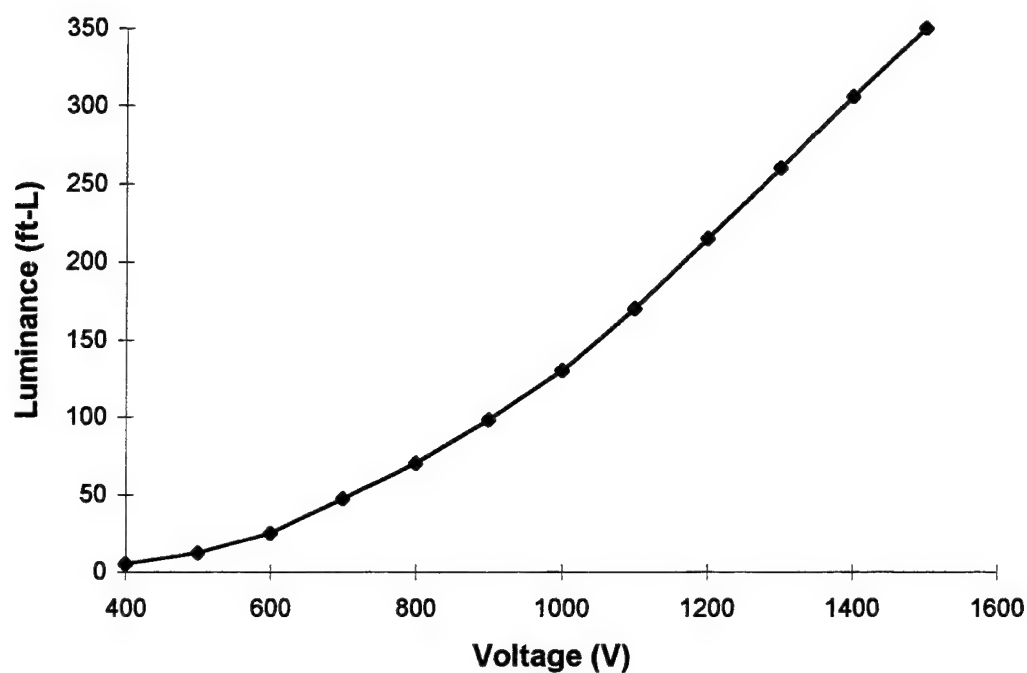
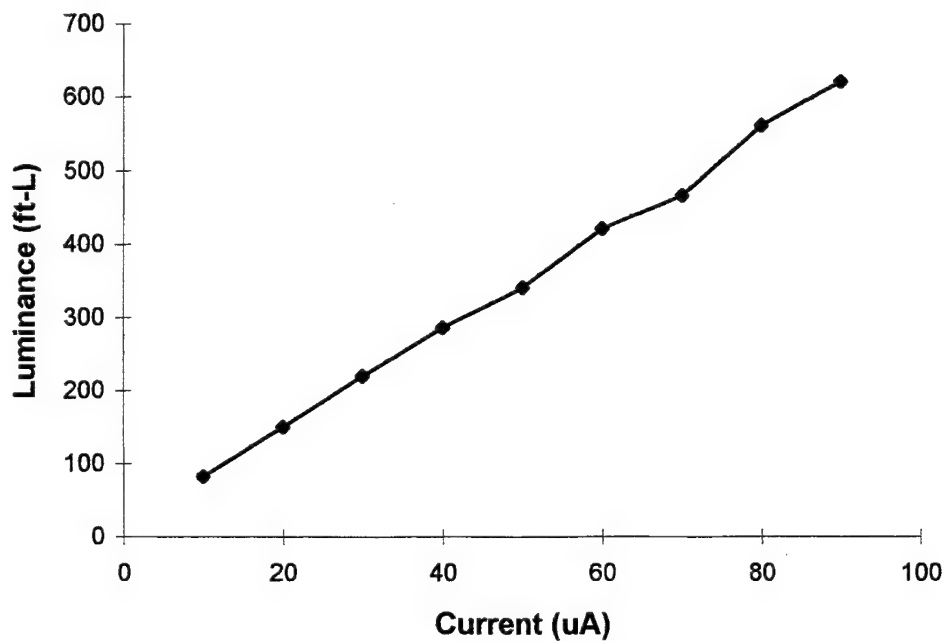


Fig. 17 I/L of SnO<sub>2</sub>:Eu, e-beam 1.41mm dia.



**Fig. 18. Luminance/Voltage Characteristics of  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  Low Voltage Phosphor, at 50uA.**



**Fig. 19. Luminance/Current Characteristics of  $\text{Ba}_2\text{ZnS}_3\text{:Mn}$  Low Voltage Phosphor, at 1500V.**

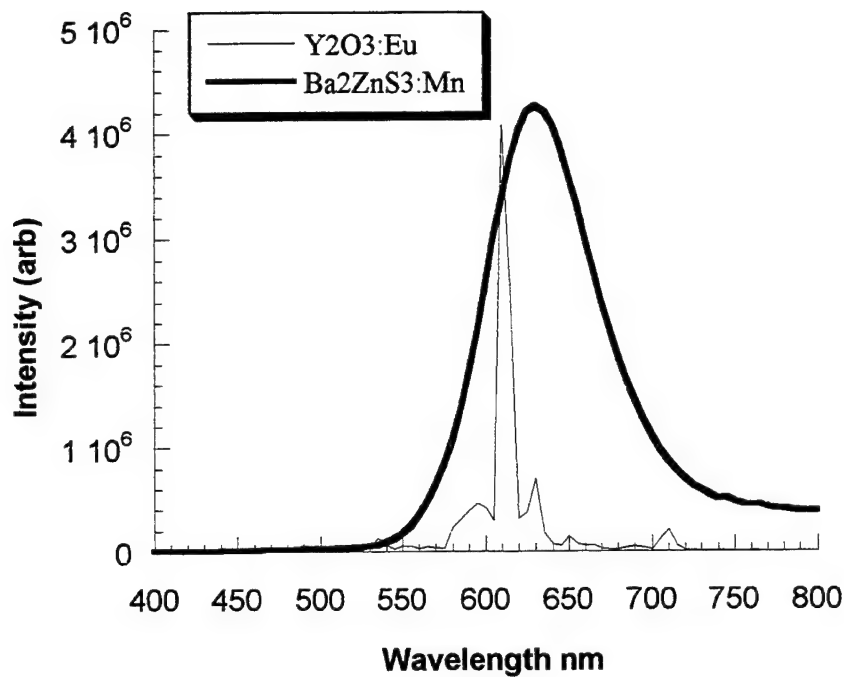


Fig. 20. Cathodoluminescent spectra of  $\text{Y}_2\text{O}_3:\text{Eu}$  and  $\text{Ba}_2\text{ZnS}_3:\text{Mn}$

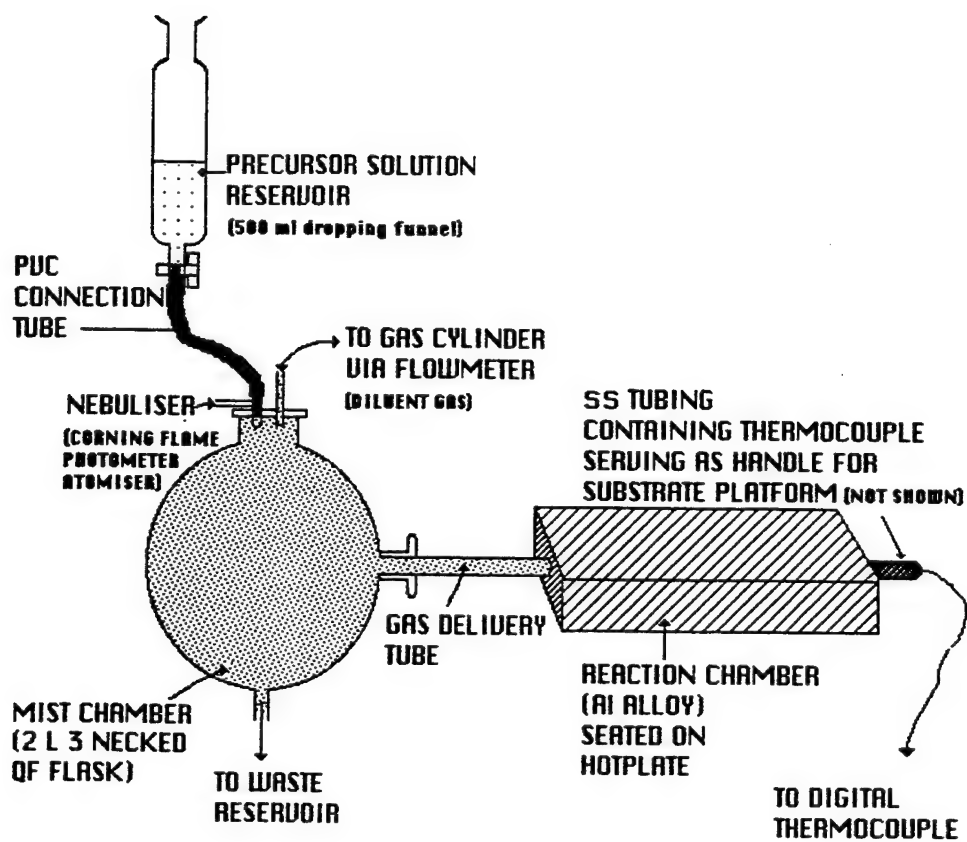
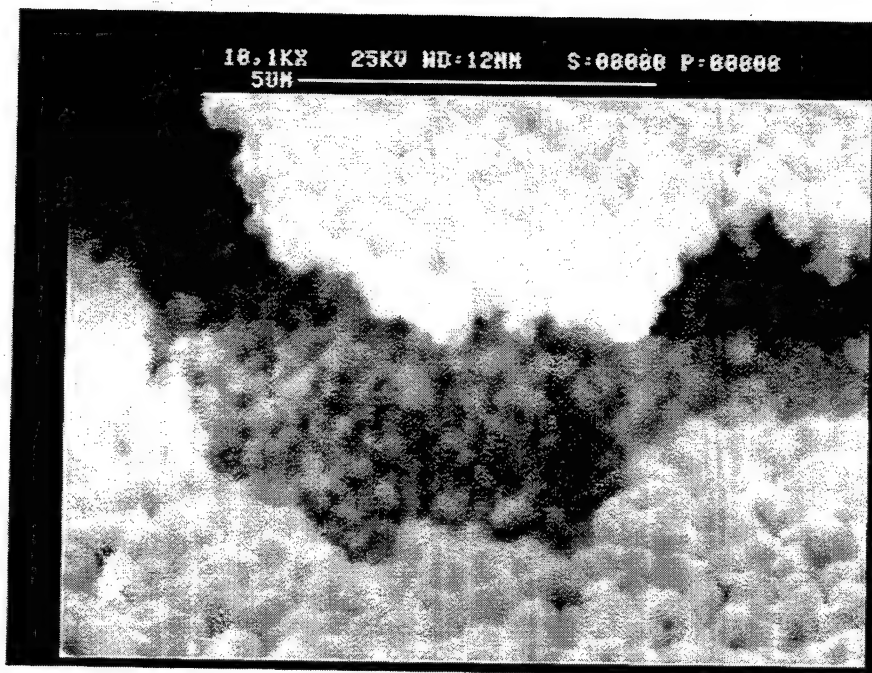


Fig. 21 Simplified sketch of the apparatus used for ASP



Photograph number 3. SEM of a 1.2 $\mu$ m ZnO:Zn thin film .

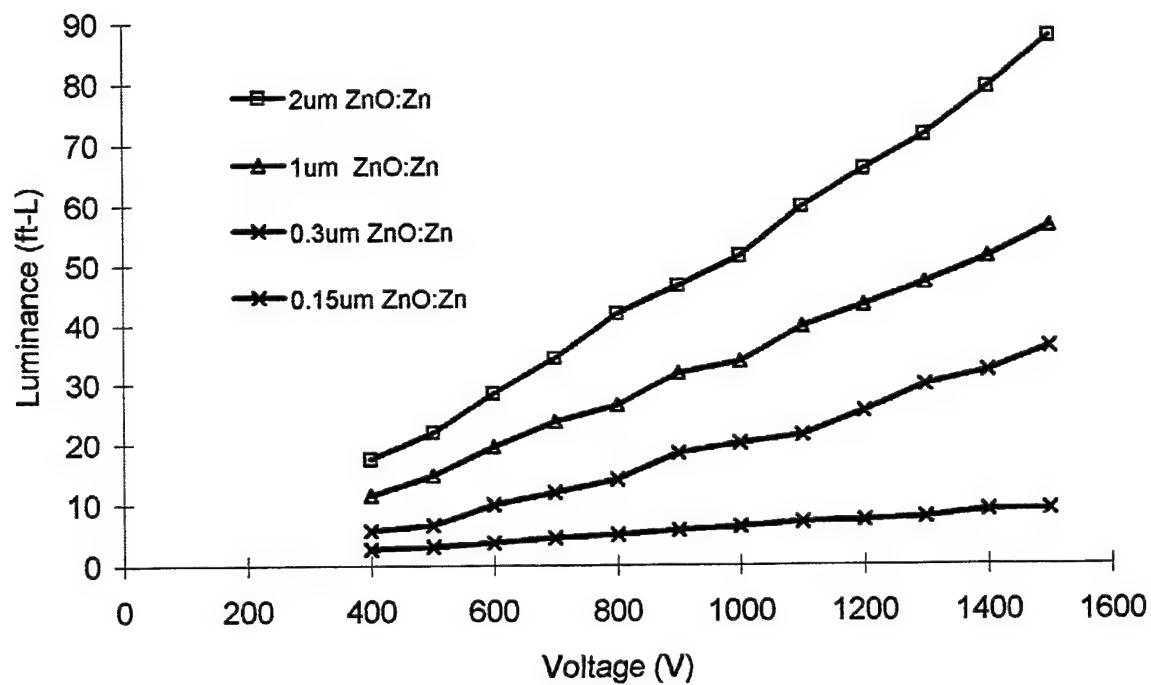


Fig. 22 V/L characteristic for simple ZnO:Zn layers, at 5 $\mu$ A, e-beam 1.41mm dia.

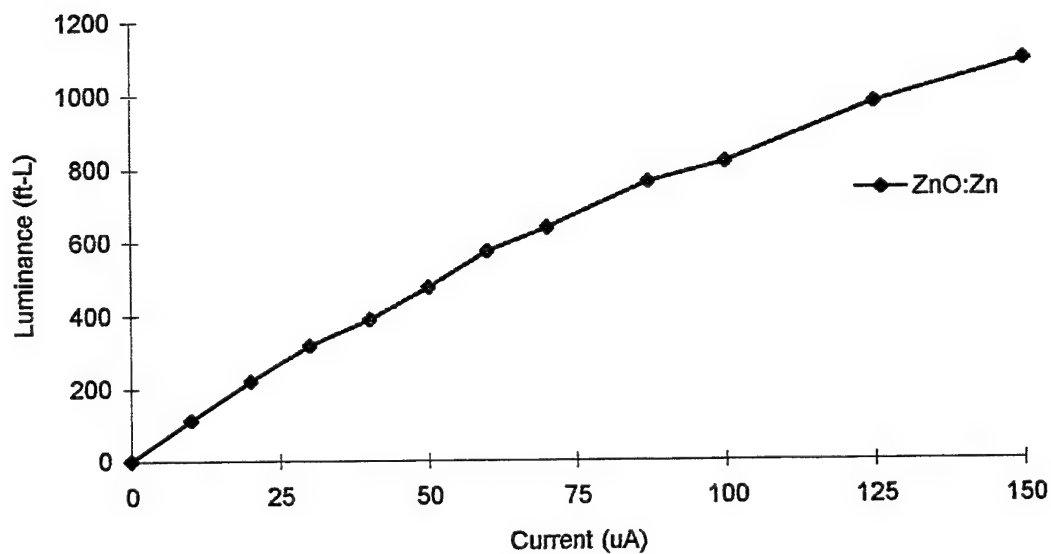


Fig. 23 I/L characteristic of ZnO:Zn thin film at 1500eV, e-beam 1.41mm dia.

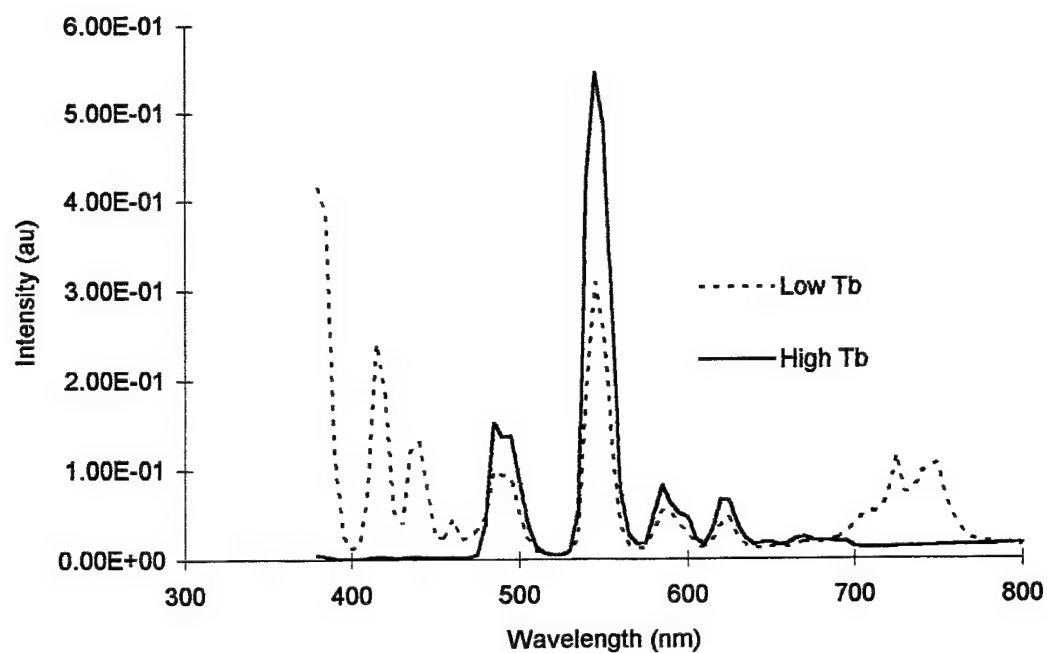


Fig. 24 Spectral emission of YAG at different Tb levels

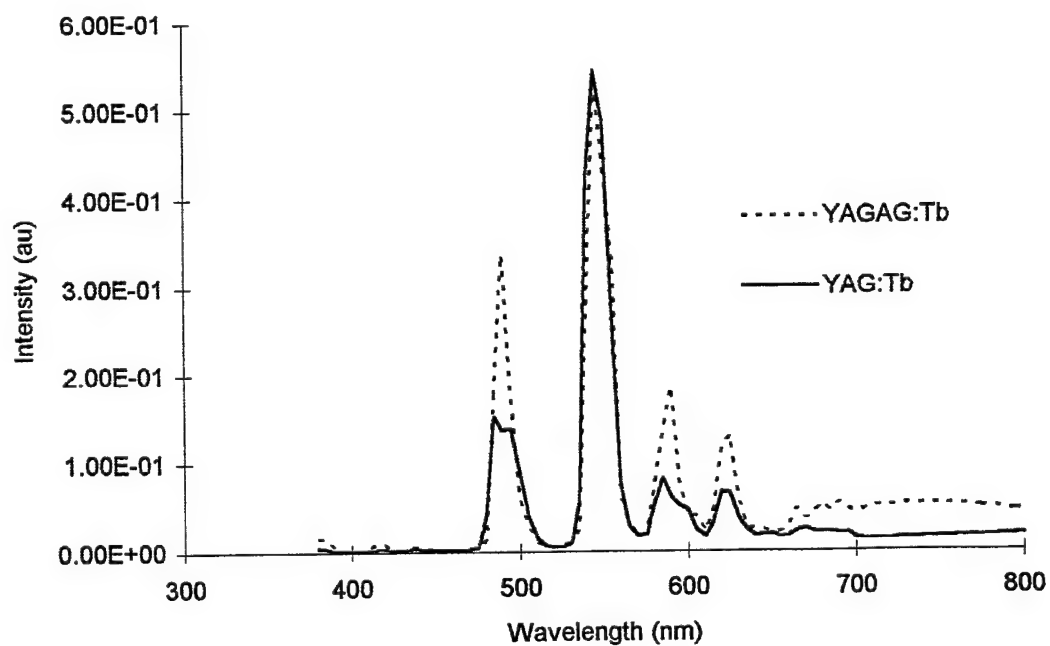


Fig. 25 CL Spectral emission of Tb activated YAG and YAGAG

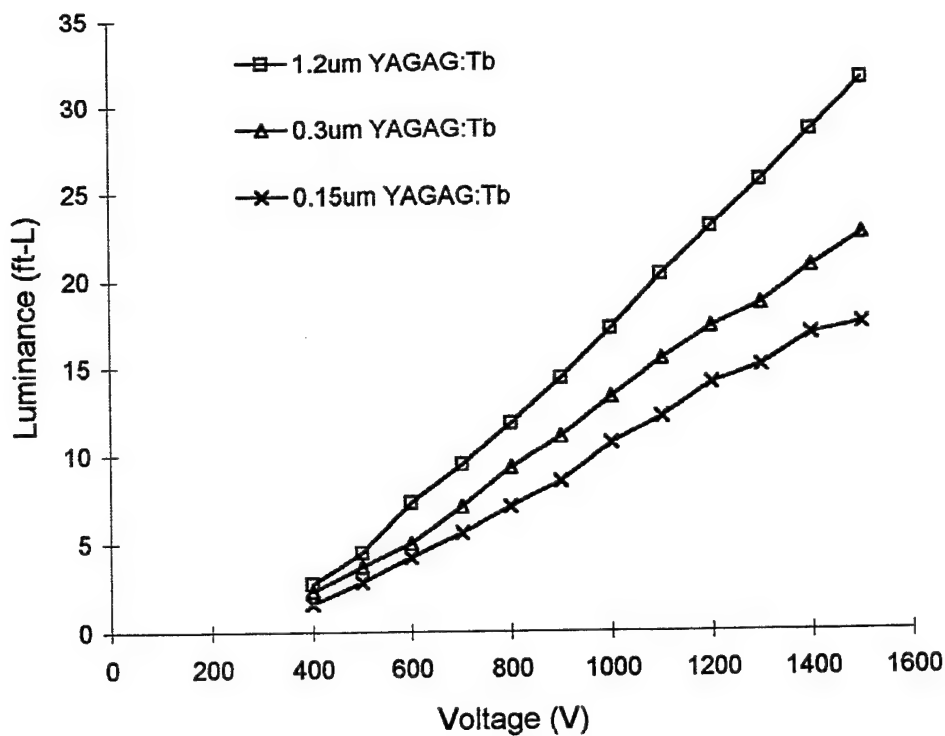


Fig. 26 V/L of simple YAGAG:Tb thin films, at 5uA e-beam 1.41mm

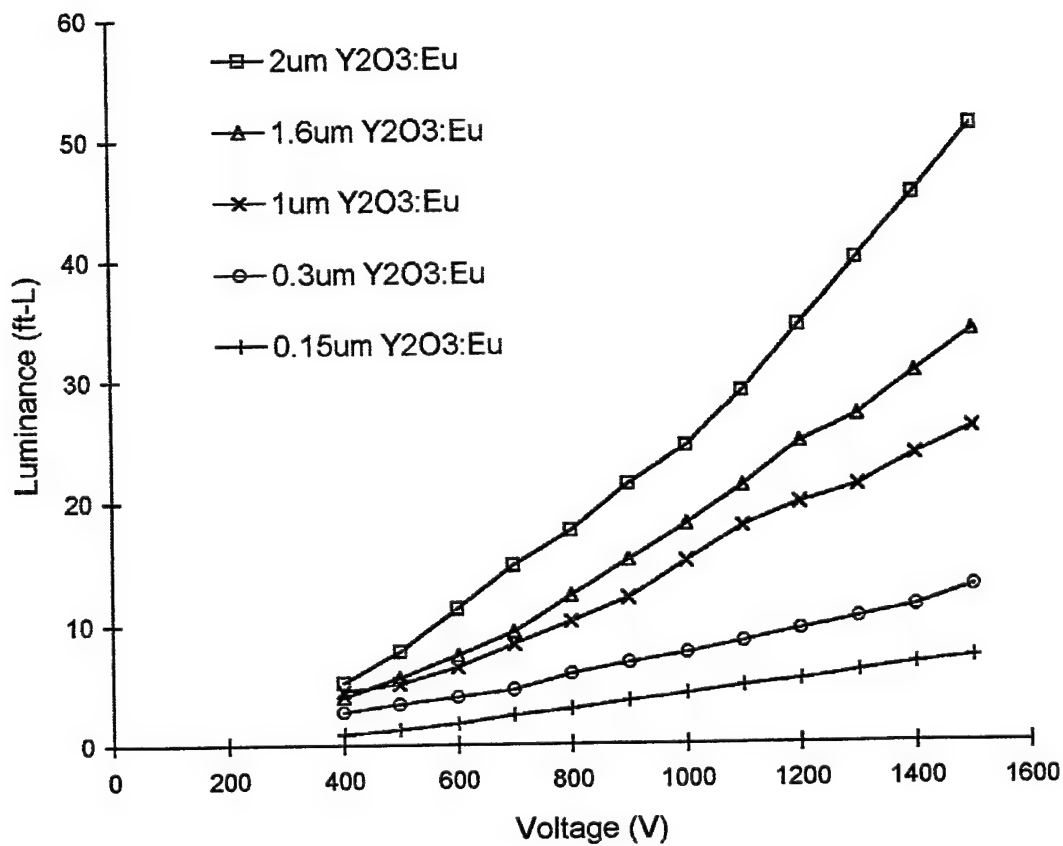


Fig. 27 V/L of simple Y2O3:Eu thin films, at 5uA, e-beam 1.41mm dia.



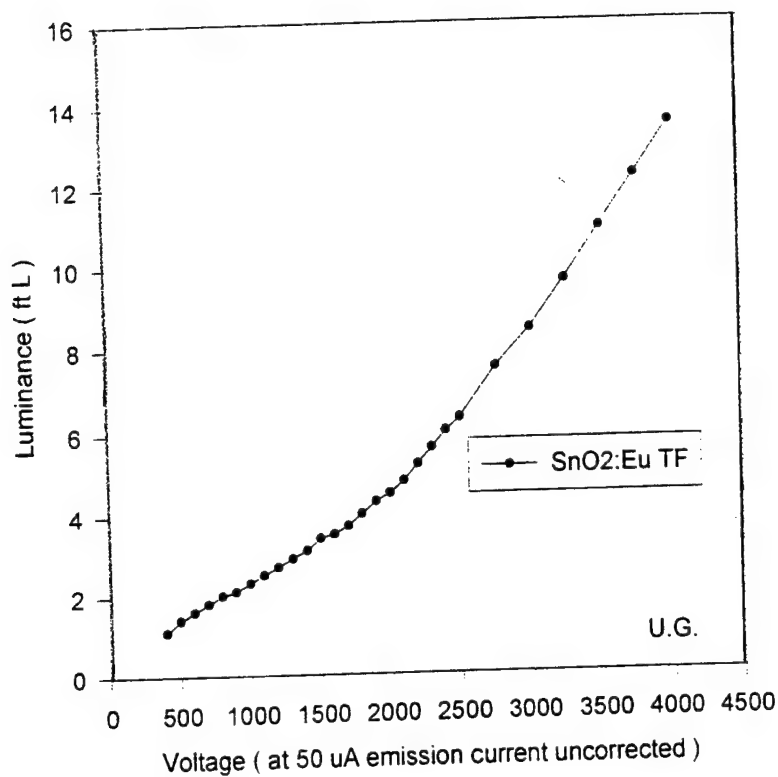


Fig. 28 V/L characteristics for SnO<sub>2</sub>:Eu phosphor thin film

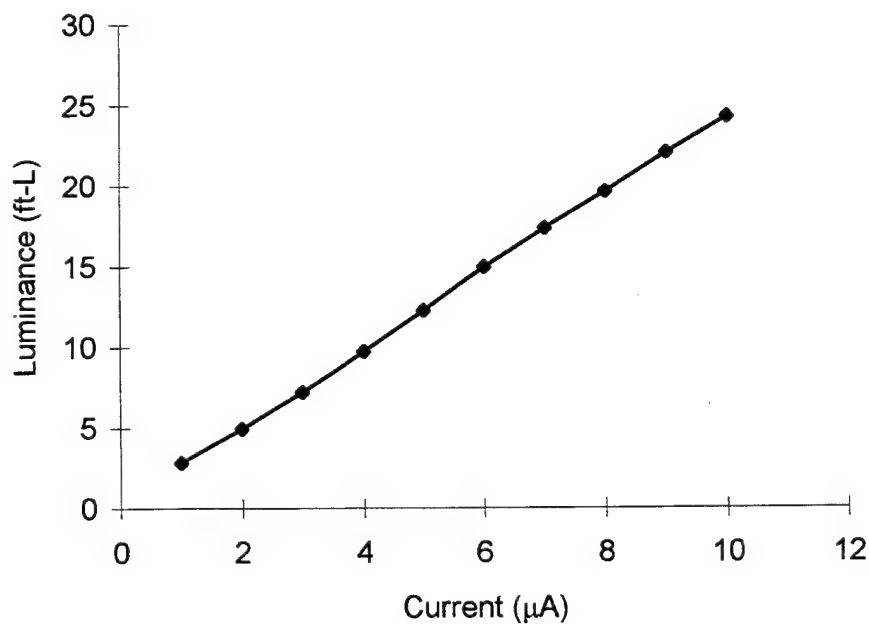


Fig. 29 I/L characteristic of YNbO<sub>4</sub>:Bi thin film phosphor, at 1500V, e-beam 1.41mm dia.

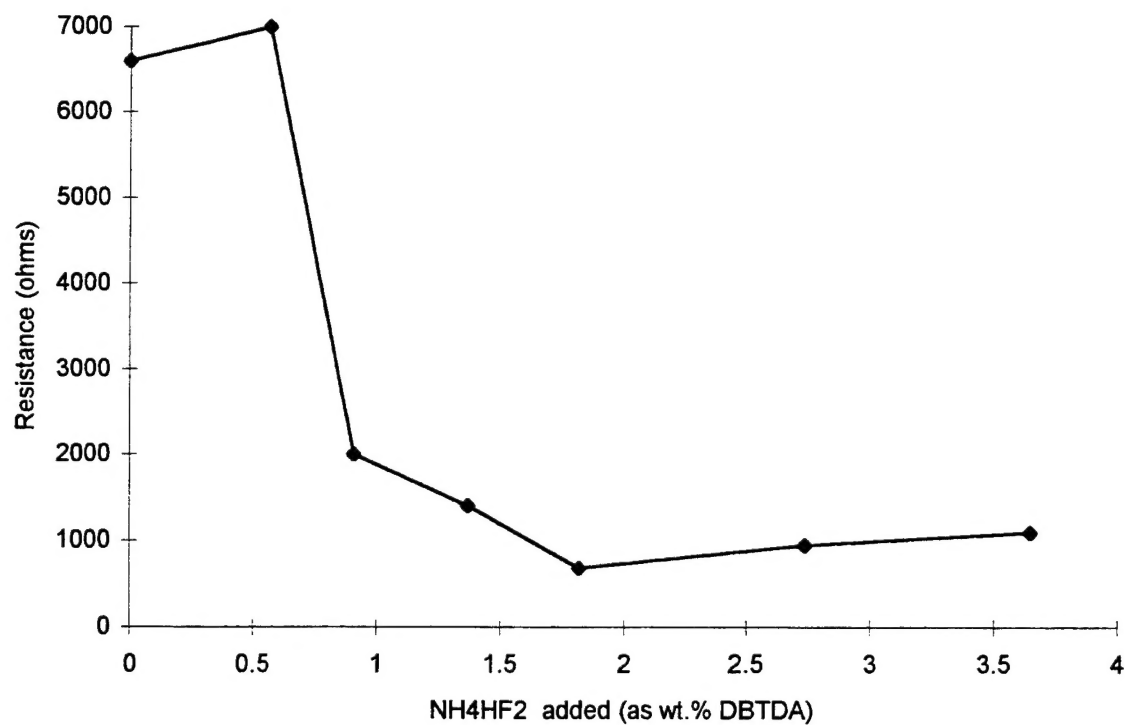


Fig. 30 Fluoride optimisation for  $\text{SnO}_2$  film

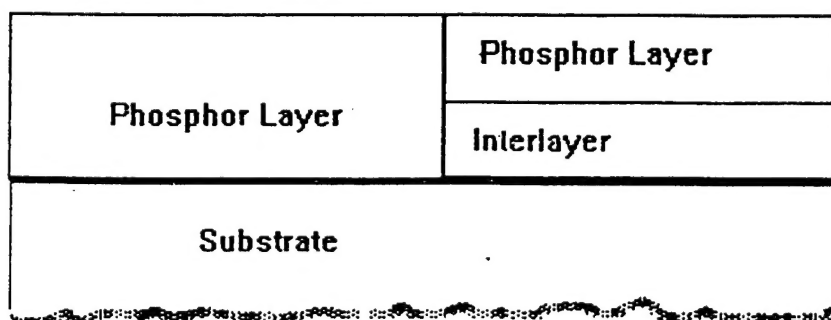


Fig. 31 Structure of a multilayer and simple layer on the same substrate

RES. SIMS PROFILE 2/9/86 S1- FEB 2 1-39.00 MIN. SPUT. ANGLE=00.0

FILE: 272a111 MER VF11, ZnO Zn/1/25SnO/61000, D. MORTON, AVA, MCN

BI= 153.00 nA BV= 8.00 kV

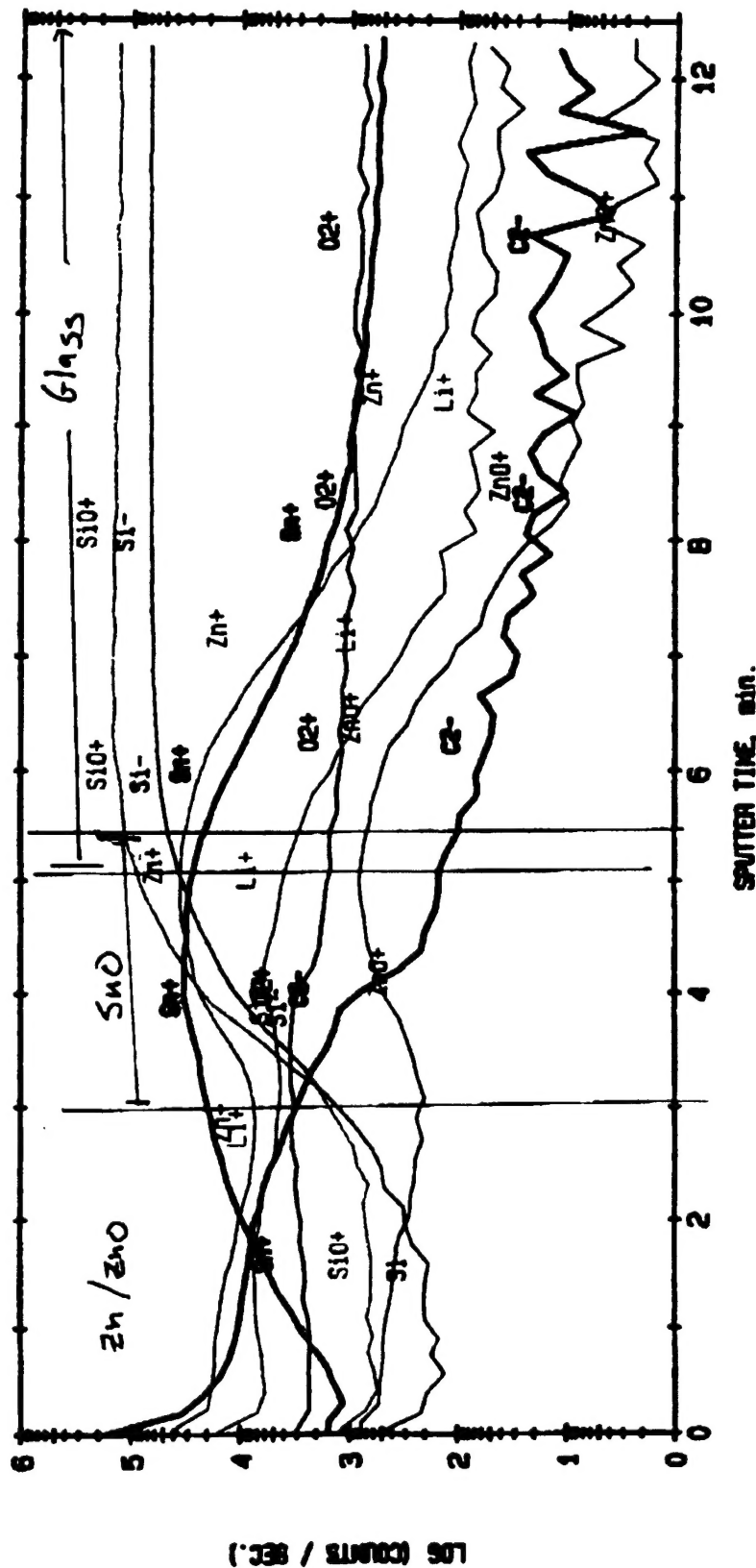


Fig. 32 SIMS data

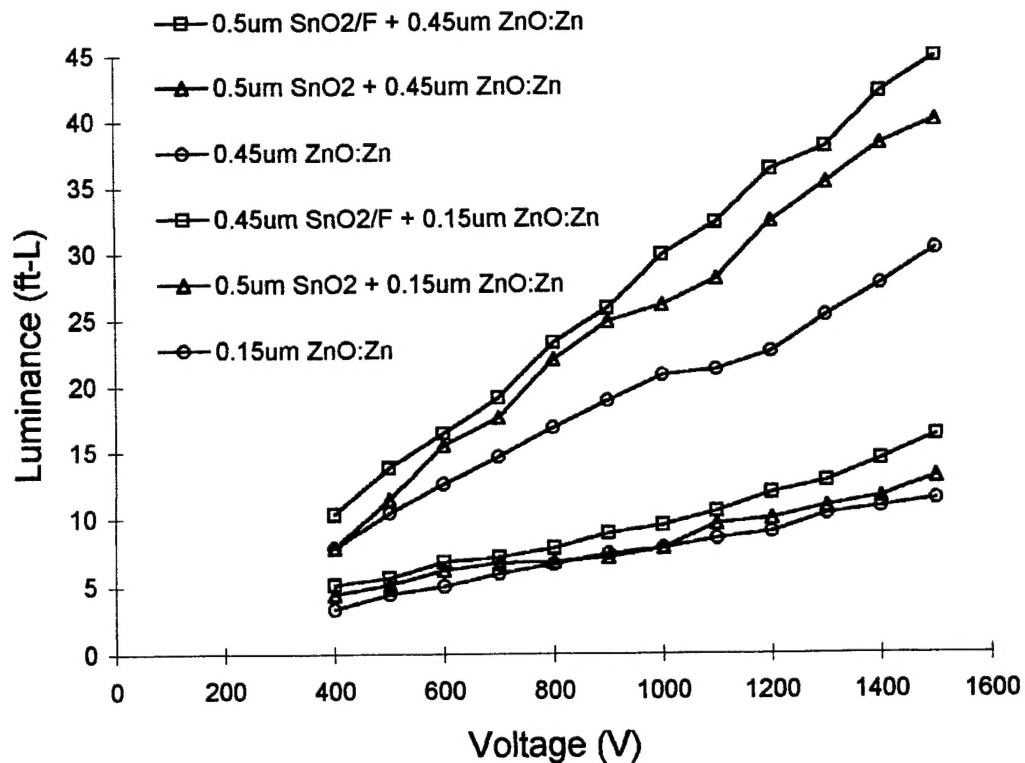


Fig. 33 V/L of ZnO:Zn multilayers, at 5uA, e-beam 1.41mm dia.

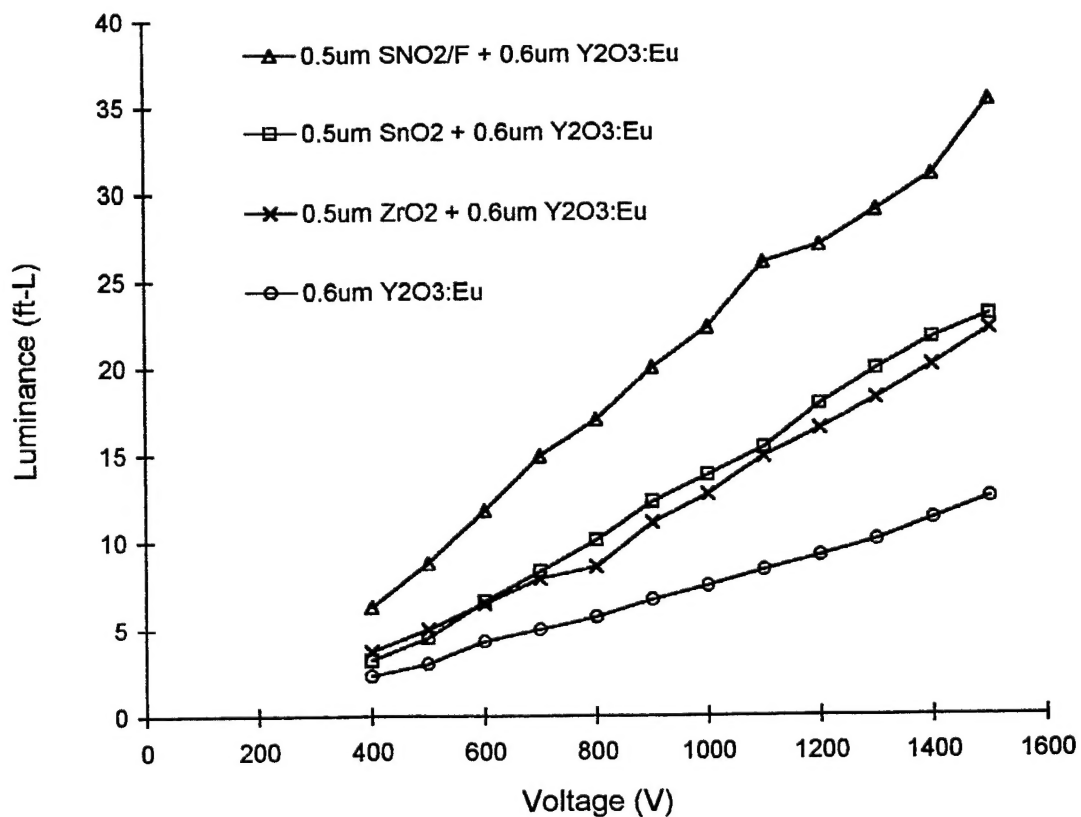


Fig. 34 V/L of Y<sub>2</sub>O<sub>3</sub>:Eu multilayer film, at 5uA, e-beam 1.41mm dia.

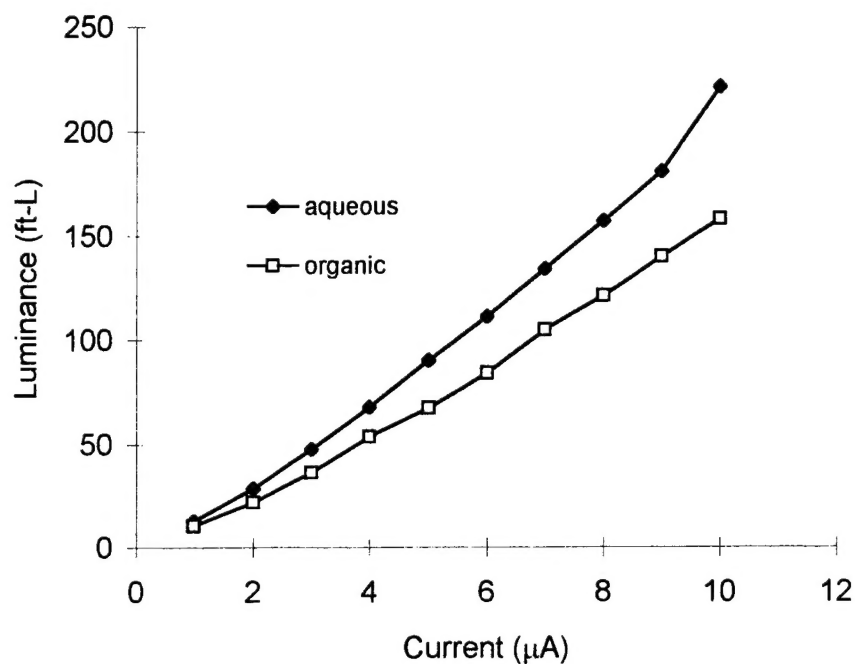


Fig. 35 I/L characteristics of ZnO phosphor thin films, at 1500V, e-beam 1.41mm dia.

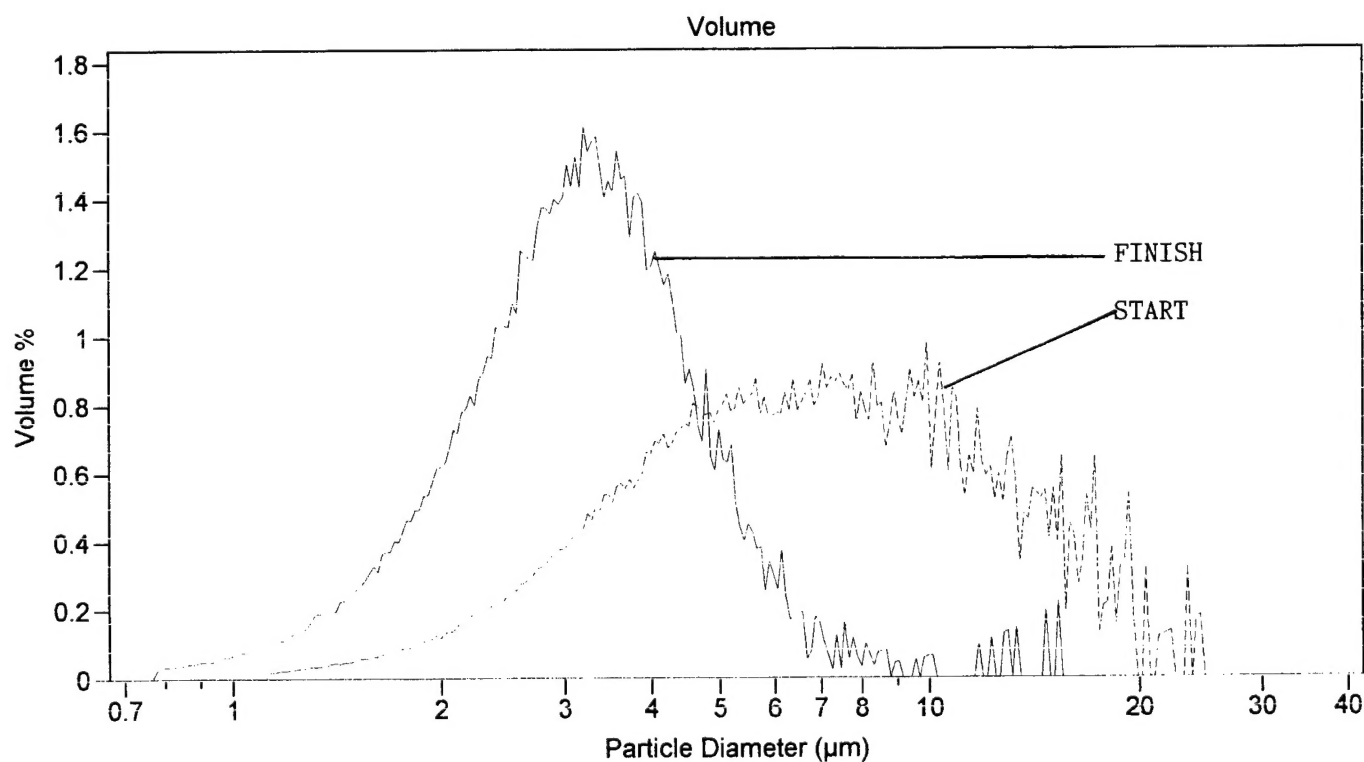


Fig. 36 Typical particle size distributions in a phosphor at the beginning and end of project.